AN EVALUATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR THE CHARACTERIZATION OF ORGANIC COMPOUNDS IN ART AND ARCHAEOLOGY

by

Gretchen Louise SHEARER

Thesis submitted for the degree of

Doctor of Philosophy

in the Faculty of Science of University College London

October 1989

Vol 1

Department of Conservation and Materials Science

Institute of Archaeology

University College London

ABSTRACT

The application of Fourier transform infrared spectroscopy (FT-IR) to the characterization of materials in art and archaeology is evaluated. The diffuse reflectance accessory was used extensively and an infrared microscope was utilized for microscopic samples. The development and theory of diffuse reflectance FT-IR spectroscopy are given and a brief outline of previous use of infrared spectroscopy in archaeological and art conservation is included. The experimental procedures and sample handling used in the research are explained in detail. Diffuse reflectance spectra of several classes of organic materials available in antiquity are presented. The classes of organic materials include waxes, fats and oils, bituminous materials, resins, amber, shellac, pitch, gums and gum resins and proteins. The spectra of the reference materials are interpreted in the light of the known information on chemical structure. Several examples of archaeological specimens which have been characterized are included. Two large groups of modern materials, a group of plastic sculptures and a collection of early plastic objects were characterized. Areas for future work include an expanded reference collection of modern materials and

the use of J-CAMP-DX programming language for interlaboratory exchange of data which is independent of the brand of spectrometer used.

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ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. N.J. Seeley, for suggesting the topic and for many hours of useful discussions. I am also indebted to Dr. D.R. Griffiths, M.M. Wright and the staff of the Institute of Archaeology Department of Conservation for help, advice and encouragment and R. White of the National Gallery for his help and for the GC/MS analyses. I would also like to thank J. H. Frantz and Dr. George Wheeler of the Metropolitan Museum of Art, Objects Conservation Department for allowing me time to finish the thesis.

The project could not have been undertaken without the support of the Victoria and Albert Museum Department of Conservation. I would like to thank Dr. J. Ashley-Smith, Keeper of Conservation, and G. Martin for allowing me to use their FT-IR spectrometer. I would also like to thank G. Martin for his advice and for many helpful discussions on FT-IR.

I am indebted to the following people for their patient help with computer work: G. Martin, D. Scouller, P. Duckworth, D. Griffiths and R. Koestler.

There are many individuals and museums who kindly allowed me to take samples for the reference collection. They are listed in the appendix.

I would like to acknowledge the financial support of S. H. Kress Foundation, the Central Research Fund, the Getty Foundation and the L. W. Frohlich Charitable Trust.

Lastly, I would like to thank my family for their monumental support over the past four years. I would also like to thank my friends and flatmates who have been extremely supportive during the writing up process, especially Sherry and Jane for proofreading.

PREFACE

The purpose of this research was to evaluate FT-IR spectroscopy for samples encountered in art and archaeology. A large number of samples of known provenance or identity were analysed to serve as a reference collection. Spectra were also obtained of unknown materials from a variety of sources and objects and attempts were made to identify the materials on the basis of their spectra.

The laboratory work was done outside the Institute of Archaeology and it was not certain at the beginning of the project how much time on the spectrometer would be available to the author. Thus, speed of sample preparation and acquisition was an important consideration. Also, the assessment of the technique was made on the basis of what might be useful to conservators and conservation students who were not analytical chemists. As a result, few pretreatment or separation techniques were carried out with the samples. The few exceptions are noted in the text. It was possible to run a large number of spectra of both reference material and unknown samples. The appendix is a catalogue of the reference materials used in this research.

The first chapter is a review of the literature of applications of infrared spectroscopy in art and archaeology. The publications concern several types of materials and applications, so the works were reviewed in chronological order. The second chapter is a review of the diffuse reflectance technique. Although little quantitative work was carried out in this research, it was considered wothwhile to include in the second chapter a brief review of the quantitative aspects of diffuse reflectance spectroscopy. This was considered to be necessary as this is the first application of diffuse reflectance to art and archaeological research. Also, this project is interdisciplinary in nature and some future workers referring to this text may not be familiar with the technique. Chapter 3 is a description of the methods used in the laboratory work undertaken in this project.

The natural products examined in this thesis are divided into five chapters on waxes, fats and oils, bituminous materials, resinous materials and proteins (Chapters 4 - 8). A brief summary of the source and composition of each material was included. The spectra of the reference materials are interpreted in terms of the band frequency assignments to determine if the spectra provide a valid means of assessing the composition of the

material. The unknown spectra which were identified are then compared to those of the reference materials. Tables of the band assignments for both reference and unknowns and the figures are located at the end of each chapter. The spectra which are presented in this thesis were reproduced using a graphics software program which assigned arbitrary values to the ordinate axis. Since the work was qualitative in nature and spectral expansion was utilized with small samples, the ordinate axis is marked in the direction of increasing diffuse reflectance (R) and no numerical values are shown.

Chapter 9 is a background chapter which discusses the history of manufacture, structure, method of production and uses of four early plastics. The next chapter analyzes the reference spectra of these four plastics and chapter 11 discusses the three groups of early plastics which were identified using diffuse reflectance spectroscopy. Chapter 12 reviews the degradtion of polymers and chapter 13 is a case study in which a collection of plastics of known date or composition are analyzed to provide a larger reference collection. Chapter 14 is a summary of samples identified as synthetic materials on archaeological objects which seem to be old conservation treatments.

CHAPTER 1 LITERATURE SURVEY ON THE USE OF INFRARED SPECTROSCOPY IN MUSEUM WORK

Introduction

A literature survey was conducted on the applications of infrared spectroscopy to archaeology and conservation. A summary of the publications is presented in this chapter. The majority of the work has been concerned with the analysis of materials used in the fine arts such as pigments and binding media. Other work has included studies of bronze corrosion products, but very little material has been published on the application of infrared spectroscopy to archaeological analysis or conservation research. An exception is the extensive analysis of amber by Beck utilizing infrared spectroscopy. The articles are reviewed in chronological order.

1953 - 1960

Infrared spectroscopy was utilized in a study of the surviving materials from Turner's paint boxes which included dry pigments, pigment pastes and three samples of either media or varnish (Hanson, 1953). The media were extracted from the pigment pastes with either tetrahydropyran or trichloroethylene. In some cases, it was necessary to saponify the sample in the presence of

alkali. The infrared spectra of the unsaponified fractions were found to be similar to those of vegetable oils. The ether-insoluble portions had spectra which were characteristic of a resin. The paper concluded that there were two types of media, one which consisted of drying oil and a resin and a second of drying oil. One of the varnish samples was identified as impure, aged turpentine and a second was identified as dammar resin in turpentine at a concentration of 68%. A third material was found to be a mixture of drying oil and resin with spectra similar to those found for the pigment paste extracts.

An early report of infrared analysis applied to studies in fine arts is given by Feller in 1954. The paper presented spectra of dammar resin (Singapore No 1) and mastic. The spectra are very similar to each other. The only difference is the presence of a band at 890 cm^{-1} in the dammar which is not apparent in that of the mastic. The spectra obtained were of cast films which were prepared from chloroform solvent. The residual solvent is thought to cause the strong band which is evident at 760 cm^{-1} and the weaker band at 1220 cm^{-1}. Samples which were dried under a vacuum gave spectra with a band of reduced intensity at 760 cm^{-1}, but the solvent bands were not completely removed.

In the study (Feller, 1954), spectra were obtained of different grades of mastic and dammar, including poor grades which were coloured. All were found to be extremely similar. Also, a sample of Batava dammar stored for 35 years was found to have a spectrum which was very similar to that of Batavia and Singapore dammars which were recently obtained. This similarity is expected as the resins are composed of the same types of constituents such as resin acids. Thus, it is difficult to obtain spectra which are characteristic for each type of dammar or mastic.

Infrared spectra were also obtained of samples which were artificially aged in a Fade-O-Meter (National Accelerated Fading Unit, Type XV) (Feller, 1954). Their spectra were measured to see if changes due to degradation could be seen in the infrared spectra. The spectra of the artificially aged materials were similar to the unaged samples in spite of the severe discolouration and cracking of the samples. The region between 1200 - 800 cm^{-1} in both types of aged resins exhibited a loss in detail. This was explained by a greater complexity in the aged material. In the spectrum of the mastic, the relative intensities of the bands at 1450 and 1375 cm^{-1} are reversed in

the aged sample spectrum. This change in relative intensities may be indicative of chemical change caused either by a decrease in the methylene groups due to oxidation or an increase in the methyl groups which result from chain scission or a combination of both. A second explanation is that the molecular environment near the groups might have been altered which would change the intensity of the group. Feller concluded that infrared may have limited use in museum work due to the difficulties in the analysis of complex mixtures and in the detection of additives in trace quantities.

The use of infrared spectroscopy was later evaluated by Feller (1959) in a review of analysis methods for resins and varnishes. The difficulties which were encountered were listed and it was pointed out that natural resins are actually mixtures of compounds and thus it is difficult to isolate small amounts of other materials. In spectra of varnish/stand oil mixtures containing 20 - 50% oil, the presence of the oil does not strongly affect the spectrum. Also, it was emphasized that aging changes the composition and that reference samples of aged standards are necessary for characterization (Feller, 1959).

Another early report of infrared analysis in conservation is the study of waxes by Kuhn (1960). The analyses were performed with a double beam spectrometer with a NaCl prism equipped with a microscope with NaCl lenses which condensed the infrared beam. In order to obtain good quality spectra, it is desirable to fill as much of the infrared beam as possible with the sample. The concentration of the infrared beam allows the analysis of milligramme and microgramme samples. In this study, the samples studied were paint media from three Fayum mummy portraits and a wall painting from Pompeii in addition to a replica of the wall painting produced using a new encaustic technique (The term encaustic means using paint in a wax medium.) The presence of pigment in the samples causes a scattering of the infrared radiation and interferences in the resulting spectra so the sample had to be separated from the colouring matter in each case. This was performed by placing the sample in a micro-crucible or in a dimpled microscope slide with chloroform for one day at room temperature. The solution was then deposited onto a NaCl cell and the solvent was removed using hot air which left the sample as a film on the surface of the cell. Benzyl alcohol was utilized to separate the wax from wax-resin mixtures

and wax may be removed from bituminous materials with warm monochlorohydrin ($CH_2OHCHOHCH_2Cl$).

In addition to the identification of the examples mentioned above, spectra were published of the following standard materials: beeswax, two relining mixtures, (one of beeswax with colophony and one of beeswax with a synthetic resin called A.W.2), carnauba wax, esparto wax, crude montan wax, stearin wax and paraffin wax (Kuhn, 1960). These are discussed in the section on waxes in Chapter 4. The substance known from antiquity as Punic wax, which was produced from beeswax, was made following an ancient recipe and spectra were published of the material and the alcohol extract.

1961 - 1970

In a further example of the application of infrared spectroscopy in the field of fine arts, the technique was used to examine the applique relief brocade from several examples of late Gothic wooden polychrome statues (Frinta, 1963). An applied material was used to imitate rich fabric and it was thought that gesso was used exclusively for this purpose. Some examples were tentatively identified as beeswax or a wax-resin mixture and

small samples were taken for infrared and microscopic examination. Infrared analysis showed that samples were indeed wax or wax-resin mixtures. It was not known before this work that wax had been utilized for this technique, perhaps because of the poor state of preservation of the relief material and the small number of pieces that have survived. The polychrome figures which were incorporated into shrines were repaired and repainted from time to time. It is thought that the replacement of the wax brocade as it became damaged may not have been possible after the skills associated with its production had become obsolete. It is likely that the wax-resin material lost its adherance to the sculpture and became brittle. Another problem resulted from successive coats of overpainting which would progressively obscure the relief. It is thought that much of the delicate brocade was lost during restoration in the late nineteenth century when the paint layers (and much of the underlying relief) were removed mechanically. Also, the beeswax would be harmed by solvent treatment to remove the paint layers. Beeswax would also be adversely affected by the wax immersion conservation techniques which are also used for statuary. This article (Frinta, 1963) illustrates two of the advantages of infrared analysis. In

addition to providing further insight into early technology, infrared spectroscopy provides a reliable method for identification of old materials before conservation to help ensure that no important information or detail is lost.

The infrared analysis in Frinta (1963) was carried out utilizing a very similar method to that ad opted by Kuhn (1960)(Mills and Plesters, 1963). The sample size was given in terms of size not weight. The size of the pieces was generally 2 to 3 mm^2, although some were smaller. Chloroform was used to extract the wax material. In this work, the solvent was warmed to facilitate dissolution of the wax and the chloroform-sample solution was centrifuged to precipitate the mineral matter. The solution was then deposited onto a NaCl plate. The solvent was evaporated by placing the NaCl disk in an oven for one hour at 110°C and the remaining sample material formed a film after cooling. The materials in the applied brocade samples were identified as beeswax and beeswax-resin mixture by comparison to spectra of known compounds. No spectra were presented in the article but reader was refered to spectra of the pure beeswax and the beeswax colophony mixture presented by Kuhn (1960).

Another early reference to infrared analysis was published by Keck and Feller (1964). During examination, a painting was found to have a coating which was observed to be insoluble in common organic solvents, water and dilute bases such as NH_4OH and NaOH. The painting was found to be extensively overpainted and the insoluble coating, which was thought to have been used to disguise the retouching, was coated with a thin film of soluble varnish. The insoluble hard material was identified using infrared spectroscopy as a high molecular weight epoxy resin of the bisphenyl variety. The article presents spectra of the unknown and of a known specimen of epoxy resin. The spectra of the samples are very similar to each other although they show very minor differences in detail. The spectra were recorded using the split mull technique which eliminates interference from the dispersing agent but requires that two spectra are measured (Chapter 2). In the spectrum of the unknown sample, two minor bands occur at 5.9 and 6.05 um which are not evident in the reference spectrum. Natural products which may have become attached to the epoxy such as oil, dammar or mastic which contain carbonyl groups are suggested as possible assignments for the band at 5.9 um. The absorption was removed from the sample

spectrum after lengthy extraction in warm chloroform. The extraction failed to eliminate the band at 6.05 um which subsequently was assigned to an imino or amide functional group. This might be caused by residual traces in the resin of the material used to cure the resin. A spectrum of a polyamide cured epoxy resin was observed to match the sample spectrum in the area fairly closely.

The authors of this article (Keck and Feller, 1964) draw the important conclusion that analytical instruments may be utilized to differentiate between original and modern materials in works of art. In this instance, analysis confirmed the suspicion that a less valuable painting had been extensively modified to resemble a more valuable one (Keck and Feller, 1964). It is now vital to be able to identify synthetic materials which have been used in conservation in the recent past as these materials have become widely available.

An extensive study has been was undertaken by Beck in an attempt to identify the source of the amber using infrared spectroscopy (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971). A large deposit of amber is located beneath the North

Sea and the material obtained from this source was widely exploited in antiquity. Secondary deposits from this source are found throughout northern Europe. Amber from these regions is refered to as Baltic amber. There are also smaller, local sources of amber which were not derived from the North Sea scattered throughout Europe. The source of amber artifacts is of great interest in the elucidation of ancient trade routes and it was highly desirable to find a reliable technique to distinguish between ambers of various sources. Previous attempts to classify the materials were not reliable.

A large number of mineralogical amber specimens of known provenance were examined with infrared spectroscopy by Beck and his collegues (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971). They established that amber from Baltic sources has a characteristic absorption pattern in the region 1250 - 1100 cm^{-1} which has not been observed in the spectra of European ambers of non-Baltic origin (Chapter 7). In spectra of weathered samples, oxidation of the material changes the spectrum and the characteristic region becomes less distinct. This important region is masked in many archaeological samples by mineral contaminants such as silicates, sulphates and phosphates

which also absorb in the the region and by the use of consolidants with strongly absorbing ester groups such as beeswax and poly (vinyl acetate). A computer program has been devised to analyse the characteristic region in order to eliminate any subjective element in the analysis of weathered or degraded samples. The computer analysis method has been found to be very accurate in identifying the provenance of mineralogical reference samples achieving a success rate of (97.5%) (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971).

Infrared spectroscopy was selected for the research into amber provenance for a number of reasons. The instrumentation was readily available and the sample size required (0.5 - 2.0 mg) was considered to be within reason. The time required to acquire a spectrum was twenty minutes which allowed a large number of samples to be analysed. Acquisition of the data was simple and did not require an experienced chemist to carry them out. Also, the resulting spectrum produced a variety of absorptions which might act as characteristic markers (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971).

Beck also emphasized that the technique is merely a

fingerprinting system which has been shown to be a statistically valid way of distinguishing Baltic amber from non-Baltic amber. The only difficulty is with badly degraded specimens which exhibit spectra which are not clear in the characteristic region. The system is not dependent on extensive knowledge of the chemical structure of amber (Beck et al., 1978).

In 1966, a review article of infrared spectroscopy in museum research was published which presented some of the work that had published and outlined several areas for possible future research (Olin, 1966). The article reported several results from the author's laboratory (Conservation Analytical Laboratory, Smithsonian Institution) obtained on a Perkin-Elmer model 521 dispersive spectrometer equipped with optics that allowed measurements to 200 cm^{-1}. The instrument was also fitted with a Perkin-Elmer dual beam condensing system which provided a sixfold demagnification of the infrared beam. The beam condenser could be utilized to perform differential spectroscopy with microsamples.

The article (Olin, 1966) reported the identification of two samples, one of which was a paint varnish layer which was

insoluble in organic solvents and the other an unknown adhesive. The varnish sample was found to have a spectrum which was indicative of a protein material and lacked bands which would be expected of natural and synthetic varnishes. It was also found to be soluble in water which supported the identification of animal glue. The second sample was found to be shellac: this information was useful in selecting the conservation treatment. Both samples were characterized as KBr pellets and the sample size was reported as 0.1 mg.

The article (Olin, 1966) also gives an example of identification of materials using comparison of unknown spectra to those of known samples. A sample spectrum of an unknown corrosion product was found to compare well to that of sampleite which is a copper phosphate complex. This identification was aided by the extended low wavenumber capability of the instrument (200 cm^{-1}) which is useful for inorganic analysis. Olin believes that infrared spectroscopy is a useful adjunct to x-ray diffraction analysis which is not always sufficient for conclusive characterization of an unknown. The spectra of natural cochineal from the coccus cacti and commercial "madder lake" which was composed of synthetic alizarin were compared to illustrate the possible

applications of the technique in textile analysis.

Olin also suggested that the differential technique would be useful in the identification of the colouring agent in the pigment maya blue. The material had been found to consist primarily of attapulgite which is a white clay. Conventional infrared spectroscopy was found to be insufficiently sensitive to identify the colouring matter and no results were reported. Infrared spectroscopy was also recommended for analysis of pigment mixtures and pigments of different shades which have identical elemental composition such as Naples yellow. It was also suggested that natural and synthetic ultramarine could be distinguished by their infrared spectra. It was also mentioned that a microsampling stategy was being developed to perform X-ray emission, X-ray diffraction and infrared analysis on a sample of 50 ug or less, but no further details were given. The review also refers to the work of Kuhn (1960), Keck and Feller (1964) and Beck and his collegues.

The article (Olin, 1966) suggested several worthwhile roads of enquiry, but only a few actual results and spectra were published. The review does illustrate the potential of infrared

spectroscopy for comparison of unknown sample spectra to those of known standards and for the differentiation of synthetic and natural materials. The conclusion does make the important point that the success of the technique relies upon obtaining a large quantity of reference material and that specific analytical procedures need to be developed for the types of samples encountered in art and archaeology. Olin predicts that infrared spectroscopy will become more important in the future analysis of paintings and historical and archaeological materials.

In a paper by Masschelein-Kleiner et al. (1968), infrared spectroscopy was incorporated into an analysis programme for old varnishes, media and adhesives. The scheme utilized solubility tests, infrared spectroscopy, thin layer chromatography (TLC) and gas chromatography. The system separates the samples first on the basis of solubility and then infrared spectroscopy is utilized to determine the functional groups present. The addition analytical techniques are used to confirm the results of the infrared analysis and to make a more detailed identification. The article acknowledges the difficulties inherent in this type of study, the small sample size available and the chemical complexity of the materials. The samples were analysed after

solubility tests as solid materials in KBr micropellets. The spectra were recorded using a Perkin-Elmer 221 spectrometer with a beam condenser which creates a sixfold demagnification of the beam.

Two case studies were given of water soluble samples (Masschelein-Kleiner et al., 1968). Three water soluble substances from an Egyptian sarchophagus were thought to be polysaccharides as the infrared specta were reported to contain bands due to hydroxyl groups and no evidence of the peptide linkages which result in characteristic bands. A second example was given of a water soluble material which was thought to be a protein based on the infrared spectrum which exhibited bands at 1640 and 1540 cm^{-1} which are characteristic of the peptide bond (Chapter 8). The spectrum was presented in the paper.

In the classification scheme (Masschelein-Kleiner et al., 1968), the samples soluble in chloroform could have been waxes, resins, bitumenous materials and oils. The preliminary differentiations were made with infrared spectroscopy. Each of the four types of material is characterized by certain band frequencies which are indicative of the functional groups present. These criteria are

discussed in detail in Chapters 4 - 7 of this thesis where the analysis of natural products is discussed. Spectra were presented of the butanol extract and the chloroform extract of a resin and a wax-resin mixture. The authors acknowledge the difficulties which are encountered in the analysis of mixtures and recommend separation of components. The wax resin mixture was cited as an example where solubility differences may be exploited. The major drawback of this approach is that it is geared to the identification of materials which have not been severely altered over time and no provision was made for identification of degradation products (Masschelein-Kleiner et al., 1968).

Another paper from the same laboratory (Masschelin-Kleiner and Heylen, 1968) presented the analysis of natural red dyes and the infrared spectra of lac, brazilline, bois du Bresil, cochineal, and carminic acid (carmine) as well as madder, alizarin and purpurin. However, the article states that the requirements for infrared spectroscopy include that sufficient sample is available to allow for extraction of the organic material. Thin layer chromatography is recommended for very small samples such as those obtained from illuminated manuscripts and paintings which

are usually too small for infrared analysis. Infrared spectroscopy was utilized with ultraviolet and visible spectroscopy to characterize red dyes extracted from wool fibres.

Similar difficulties in sample size were encountered in a study where infrared spectroscopy was utilized for the study of the materials used in illuminated manuscripts (Flieder, 1968). It was hoped to identify the materials before conservation treatment. Infrared spectroscopy was utilized to examine the organic pigments. The article presents reference spectra of several organic pigments with some spectra obtained from various illuminated manuscripts. There were major problems with the size of sample required for analysis with infrared spectroscopy which for this study was 1 mg. This amount of sample is very rarely available from manuscripts. It was not possible to identify the green colourant from a manuscript as either malachite or verdigris and analysis of purple colourants was not successful.

Infrared analysis has been included in a study of natural dyestuffs (Hofenk-de Graf, 1969). The report presents the history of use, source, composition, structure and terminology of

natural dyes such as weld, fustic, madder, cochineal, lac dye, henna and others. Several spectral methods of identification are discussed and the infrared spectrum of many of the samples are included.

A Perkin-Elmer 13 spectrometer which was fitted with the Perkin-Elmer microscope 85 was utilized in the analysis of old painting materials (van't Hul-Ehrnreich, 1970). The instrument is a single beam system because the microscope is positioned behind the monochromator where the optical path is the same for both the sample and the reference beam. Thus, the spectra also contain bands near 2360 and 1460 cm^{-1} which result from atmospheric CO_2 and H_2O vapour respectively. The microscope was flushed with nitrogen gas to reduce the atmospheric interferences. The microscope used for this project was that designed by Coates et al., (1953) (Chapter 2). The spectrometer utilized as Nernst-glower infrared source and the monochromator was a NaCl prism. The microscope was equiped with a small target thermocouple to act as a detector and the numerical aperture of 0.75 was used. The energy transmitted to the detector was estimated to be 35% of that generated by the instrument. The article also mentioned the difficulty of scattering of the light energy which often occurs

with non-homogenous sample distribution on KBr pellets or with large grains of pigment. Scattering lessens the amount of energy which reaches the detector.

Samples from test paintings and from several Dutch paintings from the 18th and 19th centuries were studied using the infrared microscope (van't Hul-Ehrnreich, 1970). Several different sampling approaches were attempted. KBr micropellets of 1 - 3 mm in diameter were prepared. However, grinding the sample with the KBr in a mortar which is the usual procedure was inefficient and some sample was lost. The second approach was to simply add the sample to the KBr in a die and press. In some cases, the microscope was used to select a layer for analysis. A third method involved dissolving the sample in an organic solvent and mixing with the KBr in a lyophilization apparatus. However, old paint samples are often insoluble. The second technique was utilized most for the study. Attempts were also made to prepare cross-sections of the samples. This is difficult for infrared spectroscopy as most resins used for conventional preparation of cross-sections are strong absorbers in the infrared. The sample spectrum would then contain strong bands due to the resin which would mask weaker absorptions and confuse the identification of

the unknown. In the study, paraffin wax was utilized as an embedding materials as it has only a few infrared absorptions. Polyethylene was also suggested as a harder material which might be useful for embedding samples for infrared spectroscopy. The sample which has been embedded is then sliced with a microtome and the resulting layers are placed on AgCl sheets in the microscope. The samples often crumbled, however. A second method was attempted to eliminate the need for a mounting material. The sample was frozen in water on a cooled microtome. The material was then sliced and the mounting material was removed by warming. However, the freezing further increased the brittleness of the sample which caused crumbling of the sample during cutting.

The detection limits of the microscope system were estimated to be 1.5 - 3 ug (van't Hul-Ehrnreich, 1970). However, the presence of atmospheric bands caused difficulties. With the sample sizes given above, it was possible to differentiate the carbonyl region from the water bands. This would indicate the presence of oils or resins, but other absorptions would be necessary to differentiate between the oils and resins. However, the bands which are used to characterize proteins such as egg white and

glue are blocked by the absorptions arising from the atmospheric water bands in concentrations of this magnitude. For old paintings, the amount of sample needed may be higher to allow for the scattering of the light. With the paraffin sections, a surface area of 37.5 by 500 um with a thickness of 20 um was found to be sufficient if the sample does not scatter a large portion of the energy. The paraffin causes problems as it absorbs in the range of the C-H stretching absorptions of aliphatic hydrocarbons (3000 - 2800 cm^{-1}). These bands may be used in a general qualitative sense to distinguish between gums, egg tempera and animal glue (weak bands) on the one hand and oils, waxes and resins (stronger bands reflecting greater quantity) on the other.

The analyses of the cross-sections from the test paintings were partially successful (van't Hul-Ehrnreich, 1970). The varnish layers were too thin to be characterized by the system as the necessary diaphragm size is too small to allow sufficient energy to pass to the detector. Also, there was a considerable amount of interference from other components. For example, the evidence of the binder utilized in the ground was completely masked in the spectrum by the absorption bands due to the chalk (calcium

carbonate). The medium could be seen in the spectrum of the vermillion paint layer as the pigment is transparent in the infrared. The results from the Dutch paintings were less conclusive. The system has the advantage of allowing the operator to see and select the portion of the sample to be analysed, which is a feature not available with a beam condenser (van't Hul-Ehrnreich, 1970). However, the inability to remove atmospheric contributions and bands from supporting media from the sample spectra lessens the advantage of the system severely.

Infrared analysis was utilized in a study of verdigris and copper resinate pigments (Kuhn, 1970). In the report, infrared spectroscopy was used in conjunction with microscopic analysis, emission spectroscopy, X-ray diffraction, X-ray fluorescence, electron probe analysis and X-radiography to characterize verdigris which is the copper salt of acetic acid. There are four different structures of basic verdigris, three of which are blue and one of which is green. Basic verdigris may contain one of the four types or be a mixture of several structures. Neutral verdigris is blue-green and has one structure. The spectra of neutral and one type of basic verdigris were given in the paper and it was reported that deviations are seen in the spectra of

basic verdigris when varying compositions are analysed. The presence of verdigris in paint samples was indicated by the presence of a band in the region 1560 - 1610 cm^{-1} which has been assigned to the ionized carboxyl group. It was reported that 30 - 100 ug of paint sample are required for detection when ordinate scale expansion and a beam condenser are utilized. The article lists the results from paintings.

Copper resinate is composed of the copper salts of resin acids and its identification is somewhat difficult (Kuhn, 1970). The material appears as a transparent green glaze which does not exhibit distinct particles when examined by microscope. TLC and gas chromatography were suggested for identification and the results of infrared examination were reported. 0.1 mg of sample was prepared as a KBr micropellet. The spectra contain a characteristic absorption near 1600 cm^{-1} which is assigned to the ionized carboxyl group. Unfortunately, this is also a characteristic absorption for verdigris and copper resinate when mixed with verdigris and consequently copper resinate may not be identified with certainty by infrared spectroscopy alone. Also, it is necessary to mention that verdigris forms copper salts of fatty acids when mixed with oil media and the infrared spectrum

of this material exhibits a broad band in the region of 6.2 um. The spectra also contain bands at 1710 and 1240 cm^{-1} which were assigned to the carboxylic acids and the resin acids. The spectrum of copper resinate prepared by a procedure dating from the 16th century was compared to material from a commercial source. The probable preparation method of the commercial sample was thought to be the treatment of a copper salt solution with and aqueous solution of sodium resiate or by melting resin with reactive copper salts (Kuhn, 1970). It is interesting that the commercial material gives a spectrum with more detail most notably in the region 1500 - 1400 cm^{-1} where three distinct bands are visible in addition to the other bands which were mentioned as characteristic of copper resinate.

1971 - 1980

Infrared spectroscopy was utilized in conjunction with a report on the conservation treatment of wax sculpture (Murrell, 1971). The study included two case studies of an allegorical tableau and two 17th century ecclesiastical dolls. Wax has been used as a modeling material for polychrome relief portraits, tableaux, anatomical models and wax dolls. The author of the article believed that most wax sculptures were contructed with beeswax

which was unadulterated except for bleaching and the addition of pigments and inert filler material. Recipes survive for beeswax mixtures in which substances such as Venice turpentine, animal fat or pitch were added as plasticizers, but the author stated that these mixtures were utilized for modeling objects such as medallions at room temperature and seldom for finished wax sculptures. It was also suggested that an additive such as resin was incorporated to produce thin sheets for draping effects. However, no extensive analytical work had been performed on wax models and sculpture which would confirm the theory. A small number of samples were analysed for the Murrell study (1971) by Mills and Plesters at the National Gallery, London. The samples were identified using infrared spectroscopy and microscopy and the pigments and inert materials were characterized by chemical tests. Ten samples were taken from four pieces with dates that ranged from the 17th to the 19th centuries. Seven samples were found to contain beeswax and pigments only and three were resin wax mixtures. Two of the mixed samples were from wax used to attach pieces in the tableau and the third was a green wax which gained its colour from copper resinate. Although it is not stated, it is assumed that the methods used and the criteria for

identification were similar to those given in the earlier reference (Mills and Plesters, 1963).

In a rare example of analysis of archaeological samples, infrared spectroscopy was utilized in conjunction with thin layer chromatography and gas chromatography to identify the contents of two Roman glass bottles as a partially degraded oil (Basch, 1972). The bottles were found in Jerusalem. The results obtained in this study are discussed in detail in the section on fats and oils.

Infrared spectroscopy was recommended as basic equipment for museum laboratories which may have to examine organic materials in a paper presented at a conservation conference in 1972 (Mills, 1972). The technique was described as particularly useful for the analysis of waxes. The sample preparation was described previously by the author (Mills and Plesters, 1963) by which the wax is extracted from the sample mixture with chloroform and then dropped onto a NaCl disk. The solvent was removed by evaporation and the spectrum is acquired from the solid residue. Several examples of wax identified with infrared spectroscopy were presented including wax from an Egyptian sarcophogus, a Roman

candle, a medieval seal and a 19th century tableau. The spectra of these samples which are of varying antiquity ranging over several thousand years are very similar to that of fresh beeswax. The material is very stable over long periods of time which permits easier identification. Beeswax and later paraffin wax were used in restoration, so care must be taken in deciding if the material is original.

Several case studies were discussed (Mills, 1972) in which mixtures of waxes were analysed. Several sculptures which date from the 19th century were found to be made of hydrocarbon wax (Chapter 4) but one was found to be composed of a mixture. The initial identification was made by comparison with published spectra and then mixtures of several different proportions were prepared to obtain reference spectra. The composition with the best match was found to be ceresine wax with smaller amounts of beeswax and stearin wax. Analysis was also made of a relining wax which dates from between the First and Second World Wars to reline several very large pictures. The spectrum was found to be very similar to that of a mixture of paraffin and beeswax. However, there was a small band which was not assigned in the spectrum of the mixture. A small amount of a resinous material

was retrieved after extraction of the sample with methanol. The infrared spectrum of the extract was measured and found to correspond closely to that of an aged sample of Venice turpentine which is similar to the spectrum of the unaged compound. The band which was apparent in the original unknown spectrum was assigned to the acetate functional group of larixyl acetate which is a diterpene component of Venice turpentine. The paper also mentions that infrared spectroscopy may be used to distinguish between bitumen and pitch, but no examples were presented (Mills, 1972).

Infrared spectroscopy has been utilized in conjunction with mineralogical methods such as X-ray diffraction (Debye-Scherrer) in a study of Egyptian pigments (Reiderer, 1974). An example was given of the characterization of a white pigment, hunite ($CaCO_3 \cdot 3MgCO_3$), and the article presents frequency values for dolomite, calcite and magnesite as well as those for hunite to illustrate that various carbonates may be distinguished by their infrared spectra. Infrared spectroscopy was described as "a useful method for subdividing similar pigments because of structural differences."

A study (Birstein, 1975) was carried out to identify the media of wall paintings located in Central Asia. Preliminary studies of the wall paintings did not include media analysis. Infrared spectroscopy was utilized in addition to thin layer chromatography and gas chromatography for the characterization of samples which ranged in age from the 2nd - 1st century B.C. to 1830. Fairly large samples were taken for the analysis, 1 - 2 g. The oldest samples from the wall paintings of Manser Depe were identified as degraded protein by quantitative amino acid analysis. The protein was thought to be gelatin which would come from the use of animal glue as the binder. The remaining samples were identified as polysaccharides. These samples were extracted in boiling water and the residues were treated with both acid and base and the extracts were combined. After water dialysis, the water was removed under vacuum and the infrared spectra was obtained of the residue which was prepared as KBr pellets. The infrared spectra will be discussed in more detail in the chapter on resins and gums although it should be noted that the specific type of gum could not be isolated with infrared spectroscopy. Thin layer chromatography and gas chromatography of the materials was utilized to further characterize the

samples. It was concluded on the basis of the chromatographic evidence, that two of the samples were of cherry or apricot gum origin and the Prunoideae species were suggested as origins for two other specimens. No origin was suggested for the remaining sample (Birstein, 1975).

Infrared spectroscopy has also been utilized in conservation research problems (Baer and Indictor, 1976). Infrared spectroscopy was used to monitor linseed oil films containing dissolved metal acetylacetonates as part of a study of linseed oil-pigment model systems. A Perkin-Elmer 337 grating infrared spectrometer was used to measure samples of 3 mg linseed oil with a 10^{-3} M acetyl acetonate concentration which were held between flat AgCl disks. Measurements were made at intervals of two sets of samples which were kept at 23 and 100°C. The ratio of the absorbance at 3450 cm^{-1} and 2940 cm^{-1} was used as a measure of the relative absorbance of the samples (Baer and Indictor, 1976).

In spite of the early predictions, conventional infrared spectroscopy was not widely utilized and few applications were reported in the literature. In 1977, a study was published in

which the advantages of the recently developed Fourier transform infrared spectroscopy (FT-IR) were discussed (Low and Baer, 1977). The new type of spectroscopy was inherently more sensitive than dispersive spectroscopy and it was thought that this would overcome some of the difficulties presented by art and archaeological samples, namely the small size and the chemical complexity of the substance. A description of the FT-IR system was given and compared to conventional dispersive infrared spectroscopy to emphasize the advantages of the new technique. Sample spectra were presented of a variety of pigments which were powdered and placed between KBr disks. It was recommended that liquids be analysed as film between KBr disks. Transmission spectra were then obtained of the powders and the films without further sample preparation. The spectra which were published included linseed oil, indigo, madder lakes, alizarin, Indian yellow, purpurin, egg yolk, albinum and paper. The sampling technique was described as 'crude', but it was emphasized that bands due to mulling oils or possible reactions of the sample with the KBr when pellets are prepared are eliminated. However, scattering effects and sloping backgrounds are often observed in the spectra of powdered materials prepared in this manner. When

significant expansion of the ordinate scale is required, the sloping background causes difficulties. The quality of the spectra in terms of high resolution, low noise and minimal sample preparation was emphasized.

The article (Low and Baer, 1977) presented the 'trading rules' which can be exploited with FT-IR. The distance of the moving mirror, the sample size and the total time required to collect the multiple scans are factors which may be "traded". The time required for one scan may be increased by increasing the displacement of the mirror to increase the signal-to-noise ratio (SNR) for the analysis of a small sample. However, the SNR may be improved by multiple scanning which lenghthens the total time required to measure the sample spectrum, but improves the spectrum. This is also advantageous for the analysis of small samples. Spectra of Indian yellow were used to illustrate the refinement of weak and overlapping bands with increased resolution. Another example shows the reduction in spectral noise with multiple scans in spectra of indigo. FT-IR was also used to examine the effects of ultraviolet radiation on films of linseed oil. Spectra of various madder lakes are utilized to point out that even in spectra where the bands may not be assigned with

certainty, it is possible to use the infrared traces as fingerprints of the compounds. The article concludes with an illustration of the improvements in SNR which can be obtained in much shorter time periods. A scan which may be obtained in one hour with FT-IR would require almost two weeks with conventional infrared spectroscopy to obtain the same SNR (Low and Baer, 1977). The article provides a very good summary of the FT-IR technique which illustrates its advantages. However, it does not actually show results from objects which would illustrate a 'real-life' situation.

The studies which have been published since the publication of "Application of infrared Fourier transform spectroscopy to problems in conservation", (Low and Baer, 1977), have been largely concerned with pigments and painting materials. Low and Baer followed up their review of FT-IR with two conference presentations on the application of FT-IR (Low and Baer, 1978a; Low and Baer, 1978b). In the first paper (Low and Baer, 1978a), the FT-IR spectra of dammar and mastic, which were prepared as films cast from chloroform onto KCl plates, were compared. The paper emphasized that the greatly improved sensitivity of FT-IR spectroscopy results in spectra with greater detail. The spectra

which are presented are similar in many respects especially in the strong bands. However, variations are observed in the shape of the bands, shoulders and relative intensities. Also, the region 1500 - 800 cm^{-1} was found to vary considerably between samples and seven sample spectra were presented. Also, the spectrum of an artificially aged resin was compared to that of the fresh material and differences are evident. Low and Baer point out that very little research has been performed on specific explainations for the differences in the spectra. The spectra which may be obtained with FT-IR are useful as unique fingerprints for each sample and it is hoped that further work may include study of aging and light exposure. FT-IR may possibly be used to determine the source of resins. This work improves upon the gloomy conclusions reached by Feller in 1954 when less sensitive instrumentation was used. The work concluded with a similar prediction to that made in their earlier review (1977) that FT-IR would become more widely utilized in museum work. The paper concentrates on the technique and does not present examples of identification of naturally aged samples.

A further report was made of FT-IR applied to the study of pigments (Low and Baer, 1978b). It was emphasized that sensitive

instrumentation is important to obtain fingerprint spectra of materials which have similar chemical structures. An example is given of three anthraquinoid lake pigments, two of which exhibited similar spectra which require minor spectral details to be differentiated. A second example was presented of several alizarin lakes. It was shown that pure Ca-Al-alizarin complex, the same material on an alumina base and a K-Al-alizarin compound on an alumina base exhibit very similar spectra differentiated only by small variations in the spectra. A sample of pigment was shown to be more similar to that of the Ca-Al-alizarin deposited onto alumina than the other two in terms of the minor features in the spectra. It is emphasized that various alizarin mixtures exhibit identical spectra when analysed with less sensitive, conventional spectrometers. Low and Baer conclude with the observation that published spectra which have been obtained using less sensitive spectrometers are inadequate in light of the spectra of high resolution and precision which may be recorded with FT-IR. Thus, new reference collections should be accumulated of pigments and other materials of interest in art and archaeology using uniform conditions and sensitive instrumentation (Low and Baer, 1978b).

An alternative sampling technique has been suggested for the analysis of small samples in conservation work (Laver and Williams, 1978). A diamond cell is used to analyse small samples by utilizing pressure to spread the sample into a thin layer. The method has been used with sucess (Laver and Williams, 1978), although the application of high pressure may result in alterations to the sample structure which may affect the spectrum.

A paper was published by Newman (1980) which analysed several pigments which were somewhat difficult to analyse using X-ray diffraction. An example was presented of a synthetic organic pigment, phthalocyanine blue which occurs in two different crystal forms. The alpha and beta forms may be distinguished by the strong band which occurs at 723 cm^{-1} in the alpha form and at 730 cm^{-1} in the beta polymorph. The spectra of pigments containing polyatomic ions were discussed. The study included several examples of chrome or Brunswick green pigments which are actually mixtures of Prussian blue, chrome yellow and often $BaSO_4$ or kaolinite which were utilized as extenders. The pigments were identified using infrared spectroscopy. A distinctive characteristic is the presence of a band in the region of 2080 -

2070 cm^{-1} which is indicative of the carbon-nitrogen triple bond in the ferrocyanide ion $Fe(CN)_6^{4-}$. This is a fairly distinctive feature which is not characteristic of any other common organic or inorganic substance and permits the detection of Prussian blue even when present in small amounts. The report also lists the absorptions which result from the CrO_4^{2-} ions which may be masked by the presence of large quantities of sulphate ions. Infrared spectroscopy may be used to differentiate between the two forms of green earth pigments, celadonite and glauconite. A spectrum from an sample taken from a painting is presented which is difficult to interpret. Band assignments for carbonate ions, sulphate ions, alpha-SiO_2, green earth pigment and a possible proteinaceous medium are suggested, but further analysis such as microscopy were recommended for confirmation of the identity of such samples and the infrared spectrum should not be used as conclusive evidence. The pigments Cr_2O_3 and veridian ($Cr_2O_3 \cdot 2H_2O$) are amorphous and each exhibit characteristic absorptions in the region 800 - 400 cm^{-1}. Newman concludes that infrared is a useful technique in the analysis of materials used in art, but is somewhat less useful for actual painting samples

due to difficulties in characterizing mixtures and the size of the sample required.

1981 - 1988

A relatively recent application of FT-IR in conservation research is the characterization of corrosion products. A study was presented of the components of Bronze disease (Tennent and Antonio, 1981), copper chloride, which exists as a mixture of materials which have the identical chemical composition but different structures, namely, botallackite, paratacamite and atacamite. Although infrared spectroscopy was not widely used for corrosion products at that time, the extended range which allows analysis in the far infrared suggested its use for inorganic materials. Conventional dispersive infrared spectroscopy was utilized to characterize synthetic corrosion products which were produced in the study by comparison to those obtained of mineralogical standards. It was found to be and effective technique to differentiate between the three polymorphs which were of known identity. The spectra were published and the frequencies and band assignments were given. It was reported that mixtures of the minerals could be detected. The further uses of infrared incorporate its ability to characterize organic

materials. For example, the reactions of the corrosian stabilizer, benzotriazole (BTA) are being studied (Tennent and Antonio, 1981).

A further report presents a large reference collection of minerals which may be found in bronze patinas (Matteini et al., 1984). It is emphasized that corrosion products are often complex, especially if the object is located out-doors. Spectra were recored with a conventional dispersive spectrometer (Perkin-Elmer 157G) with the range of 4000 - 625 cm^{-1} and the samples were prepared as KBr pellets. Sample sizes of 1.5 - 2 mg were used and acquisition times of 30 minutes are reported. The reference materials were obtained from commercial sources (analytical grade), laboratory preparation and mineralogical standards. Reference spectra included copper salts such as chlorides, sulphates, nitrates, carbonates and oxalates. Other minerals considered were quartz and silicates, calcium carbonates, oxalates, nitrates and sulphates, and lead sulphate. The paper presents the spectra and tabulated frequency data. The use of conventional dispersive spectroscopy and the inability to measure the extended range result in the loss of important detail. Also, only one reference was mentioned of specific

application, Fiorentino et al., 1982, when detection of copper nitrate on the bronze 'Door of Paradise' in Florence using infrared spectroscopy indicated that the object had been cleaned with nitric acid.

FT-IR with a microscope attachment was utilized in a report published on the examination of samples from an unattributed painting 'Virgin and Child' which was thought to date from the 15th century (Shearer et al., 1983). The article discusses the the difficulty of evaluating the authenticity of paintings which have been restored in the past or covered by old, discoloured varnish. Treatment usually includes the removal of old varnish and retouchings, and weakened areas and flaking paint need to be stabilized. The treatment may involve the repainting of missing areas and revarnishing. The necessity for conservators to identify the materials incorporated into works of art before carrying out any treatment is emphasized in the article. The ability of infrared spectroscopy to characterize both inorganic and organic compounds was emphasized in comparison to other techniques commonly used in art conservation such as polarized light microscopy, X-ray diffraction, X-ray fluorescence and electron probe microanalysis for characterization of inorganic

components and gas chromatography for organic materials. The advantages of using a FT-IR spectrometer equipped with a microscope are illustrated by the analysis of two microscope samples removed from the painting 'Virgin and Child'.

A core showing a cross-section of the paint and varnish layers was removed from the upper right quadrant of the painting and a small sample of the red material was taken from the lower left corner. The samples were collected with a scalpel and dissecting needle under a stereo zoom microscope. The samples were analysed with a FT-IR system which included a beam condenser and a wide-band mercury-cadmium-tellurium (MCT) detector (Analect fX-6201 FT-IR spectrometer and an fXK-635 detector and an fXA-510 aspheric beam condenser). The wide band detector was chosen over a more sensitive narrow band detector as it measures a wider range, down to 450 cm^{-1}. The sample preparation used in this study was that published by Cournoyer et al., (1977) in which small salt crystals are prepared by multiple cleaving of commercial crystals until plates of 1-2 by 3-4 mm dimensions and thickness of 200 - 500 um are obtained. An aperture disk is made from a sheet of brass or stainless steel which is 1 mm thick and a aperture is made with a diameter of 20 - 200 um. The sample is

placed between two cystal sheets and mounted with a small amount of wax onto the aperture disk. The sample is positioned to fill as much of the aperture as possible (Cournoyer et al., 1977; Shearer et al., 1983). The minimum sample size required for conventional infrared spectroscopy is reported to be 0.5 ug and the limits of detection are three orders of magnitude less for FT-IR (Shearer et al., 1983).

The publication includes the spectra obtained of the samples (Shearer et al., 1983). The red material was found to be shellac. The cross-section was found to have four layers. The base layer or ground was identified as calcium sulphate dihydrate, but it was not possible to identify the binder. The first paint layer was blue and the pigment was identified as Prussian blue by the appearance of a band at 2091 cm^{-1} (characteristic of the ferrocyanide ion (Newman, 1980)). The spectrum is also thought to contain evidence for the presence of natural resins. The spectrum of the second paint layer was interpreted as containing kaolinite and an organic material which was not identified. This is thought to be an example of lake red which is prepared by combining an inorganic support with a red organic substance and then a binder is added. The last layer is

a thin gilding. The spectrum is characteristic of kaolinite. This material was often used as a ground for the gilding. The gilding material is thought to be elemental gold which does not exhibit distinctive absorptions in the infrared region.

The conclusions which were reached in the study exemplify the methods used to determine authenticity in works of art. Evidence of materials which were known to have been available during the period in which the object was thought to have been produced is taken as an indication of authenticity. Also, knowledge of conservation techniques utilized in the past is used to evaluate whether the presence of certain materials might be indicative of treatment. This is necessary as it has only recently become standard practice to kept records of conservation treatment. The presence of Prussian blue pigment which was not available until after 1704 and the presence of resin as a medium indicate that the picture was heavily restored original or a copy. This supported the opinion of the art historian without the removal of large samples or other damage to the painting. The article reports that the presence of oil or resin medium also suggests a later date for the painting as egg tempera was the predominant material in use until the beginning or middle of the 16th century

when oil came to be widely used. No evidence of protein material was seen in the spectra obtained in the study (Shearer et al., 1983). Proteins are easily masked by the strongly absorbing pigments, however, and their presence may not be detected.

Infrared spectroscopy was utilized in conjunction with gas chromatography/mass spectrometry (GC-MS) to characterize six examples of pitch recovered from the Mary Rose shipwreck (Evershed et al., 1985). A sample of a tarry substance from an early medieval site in York and a further sample from an Etruscan shipwreck located off the coast of Giglio, Italy were also examined. Infrared spectroscopy was incorporated into this investigation as a preliminary technique. The samples which were adhered to fragments of rope, wood or animal hair were collected by solvent extraction with dichloromethane in an elution tube. The other Mary Rose samples were examined with no further sample preparation. The samples were examined as films cast from the melt or from the dichloromethane solution. No mention was made of sample size, but microsampling did not seem to have been used. The samples were identified by comparison to standard spectra obtained of wood, coal, peat and petroleum tars including commercial Stockholm tar which was produced from Pinus sylvestris

wood. All of the samples from the Mary Rose were observed to be very similar to each other. No spectra or specific frequency values were given, but the presence of carboxylic acid groups, aliphatic and aromatic C-H groups was reported. The sample spectra were said to resemble that of Stockholm tar very closely both in the frequency values and the relative intensity of the absorption bands. The infrared spectra of the York and Etruscan samples were reported to be similar to the Mary Rose sample spectra and that of the Stockholm tar. The Mary Rose sample spectra were also found to be somewhat comparable to the peat tar spectrum. The spectra of the petroleum bitumen and coal tar, however, were found to be dissimilar to the Mary Rose sample spectra.

A sequel to the original report on the application of FT-IR to conservation (Low and Baer, 1977) appeared in 1986 (Low and Varlashkin, 1986). In this study, the use of photothermal beam deflection spectroscopy (PBDS) was examined as a non-destructive method for the analysis of surfaces. PBDS is a type of photoacoustic spectroscopy where infrared radiation is introduced to the interferometer and then directed to the object surface. The sample surface, which is estimated to be 2 mm in diameter,

absorbs radiation which then degrades to heat. Some of the heat energy travels to the air and changes the refractive index. A helium-neon laser is utilized as a probe beam which is used to monitor the changes caused by the infrared beam. The spectrum is processed from the information which reaches the detector by a data processing program which is similar to that of conventional FT-IR and a reference spectrum of carbon is used. Examples are given of analysis of a Moroccan dagger hilt. Several inlays were identified as mother of pearl, celluloid, ivory or horn and the varnish was characterized as a cellulose coating. The technique is physically limited by the size of the sample compartment but this could be overcome in theory. The sample surface area which is analysed may be reduced with a concomitant loss of energy throughput. A serious drawback is that the sample must be extremely near the surface or the beam is prevented from reaching the detector. Inlays which were as little as 0.1 mm below the surface of the object could not be examined. The texture of the material is a factor. As the porosity increases and particle size decreases, the photothermal signal increased. For example, mother-of-pearl gives a weak signal. Smooth, non-porous samples require longer scanning times. Another problem with the method

is that the sample is heated. The temperature is estimated to reach 50°C. The PBDS technique is useful for materials which scatter or absorb infrared very strongly, materials which are difficult to study with conventional infrared spectroscopy.

Recent applications of FT-IR spectroscopy to archaeology include an extensive study of resinous materials from Southeast Asia, primarily from the Maylasian peninsula (Gianno et al., 1987). The study includes analysis of a botanical reference collection of resinous tree products which were obtained from resin producing trees from the region. The project is being carried out to gain a better understanding of trade in the region by monitoring the occurrence of resins which formed part of the economy. FT-IR spectroscopy was selected for this analysis because the large number of samples to be analysed required a fairly rapid technique. Gas chromatography and gas chromatography/mass spectrometry analysis give more information, but are more time consuming and the instrumentation is more expensive than FT-IR spectrometers. The samples were analysed as KBr pellets. The sample size used for the reference materials was 2 - 3 mg in 200 mg of KBr. The mixture was ground in a vibration mill and then formed into 13 mm diameter disks. For

the samples from ethnographic materials, 0.3 - 0.5 mg of sample were taken and mixed with 20 mg KBr and formed into micropellets. Three types of samples were examined: the extensive botanical reference collection, archaeological specimens which were obtained from four sites and samples from items from the Smithsonian Institution ethnographic collection. A cluster analysis program was developed using coefficients of similarity which was utilized to classify the spectra. The majority of the botanical samples seemed to fall into groups characteristic of each botanical family. The archaeological samples were found to fit into clusters of the reference materials which resulted in the assignment of a resin family to the unknowns and a genus characterization was also made for three of the samples. The analysis of the ethnographic samples was less successful and only a few sample spectra were found to correspond to those of the reference material. The variations in spectra between the ethnographic and the reference collections are thought to result from several factors which include conservation treatment to the objects and possible processing of the materials by the manufacturers of the artefacts (Gianno et al., 1987).

The problem of identification of bronze corrosion products has also been recently addressed (Giangrande, 1987). In this study, conventional dispersive infrared spectroscopy (Perkin-Elmer 225 double beam grating spectrometer) with an extended range of 4000 - 200 cm^{-1} was utilized. Cesium chloride was used as the alkali halide matrix. Eighteen mineral reference standards were collected and seven mixtures of known composition were prepared. In addition, 35 samples of corrosion products from objects were collected. The spectra of the standard minerals were discussed with assignment of the bands to specific bonds, vibrations or specific atomic or molecular structures. The analysis of the mixtures illustrates the difficulty encountered when bands overlap. Inorganic materials absorption bands are typically broad and the bands may overlap. Often in inorganic mixtures, bands overlap to such an extent that broad areas of absorption are observed which are not very characteristic. This is illustrated in the mixture of 75% atacamite and 25% paratacamite where the principal bands of paratacamite are masked by bands resulting from atacamite. This problem was not observed with combinations composed of malachite and cuprite as the bands which are considered characteristic do not overlap. Sucess was

reported in the identification of some of the unknowns. Spectral subtraction of FT-IR spectra was recommended for unknown mixtures. The article discusses the advantages of infrared spectroscopy over X-ray diffraction. These include the ability to measure samples which are non-cystalline in some phases, to detect water in the structure, and to identify anions such as carbonates and silicates in the structures. The speed and simplicity of the technique are emphasized and the possibility of utilizing infrared spectroscopy in stabilization research is proposed (Giangrande, 1987).

The growing interest in FT-IR in museum work is reflected in a recent conference publication (Martin, 1988) in which the technique is explained and several examples of "real life" museum applications are presented.

Conclusion

In light of the gaps which exist in the analysis of archaeological samples, the focus of this research project was placed on the analysis of organic materials which were found as or in conjunction with archaeological objects. Samples such as pigments were not included in the reference collection. As the

project progressed, it became necessary to add synthetic materials to the library as they frequently appear as a result of old or field conservation treatments. Also, objects composed entirely of modern materials are beginning to present urgent conservation problems and attempts were made to identify these materials.

In many of the papers which were summarized above, the results were quite promising. In most cases however, the advantages of infrared spectroscopy have been substantially improved by the introduction of FT-IR. For example, the study of amber by Beck and his collegues is a very good illustration of how a wide survey of a well documented reference collection may be used as a reliable fingerprinting technique and it also indicates the advantages of computer analysis in this type of work. The sample size and sample preparation and acquisition time which were more than acceptable at the time may be significantly reduced using FT-IR. However, few publications have as yet appeared using the new technique and the intial reports which rightly point out the obvious advantages do not actually illustrate their arguments with examples of analysis in practice. Thus in this work, the

emphasis has been placed on the analysis of a large number of samples from objects which have undergone a variety of degrees of degradation.

CHAPTER 2 DIFFUSE REFLECTANCE SPECTROSCOPY

Fourier transform infrared spectroscopy

The principle of Fourier transform infrared spectroscopy (FT-IR) is based on the two beam interferometer developed by Michelson in 1891. The design is basically the same for all instruments although the principle has been modified for special purposes (Figure 2.1) (Griffiths and de Haseth, 1986).

The interferometer has two plane mirrors placed perpendicular to each other. One is fixed (F) and the other one (M) moves in the direction which is perpendicular to its plane (Figure 2.1). A semi-transparent beamsplitter (B) is located between the mirrors and this reflects a portion of the light to the fixed mirror and transmits a portion of light to the moveable mirror. The moving mirror causes varying path differences which introduce an interference between the beams when they are combined. The beams return to the beamsplitter where they recombine and again are partly transmitted to the detector (D) and partly reflected to the source (S). For a single frequency and constant mirror velocity, the signal is a sine wave with the maxima occurring when the beams are in phase and the minima when they are 180° out of phase. The beam directed to the detector is passed through

the sample where portions of the radiation are absorbed, hence the intensities are changed. The spectral information obtained from FT-IR spectrometry is measured from the change in intensity of the beam directed to the detector. This variation is measured as a function of the path difference (Griffiths and de Haseth, 1986).

The signal measured by the detector is called an interferogram and the information is transformed mathematically into a spectrum using the Fourier transform. The interferogram of monochromatic radiation (single frequency) is a sine wave and the Fourier transform is a fairly simple mathematical operation. If, however, the source emits a continuum, as is necessary to obtain an infrared spectrum, the resulting interferogram is the sum of the interferograms of each wavenumber. This complex interferogram requires a digital computer to extract the spectral information and this factor prohibited the development of the technique until the computer age (Low and Baer, 1977).

An FT-IR spectrometer measures all frequencies simultaneously unlike dispersive instruments which obtain them sequentially. Thus, many FT-IR spectra can be accumulated in the time required

to measure one spectrum with a dispersive infrared spectrometer. Interferometers do not have slits which restrict the amount of energy which reaches the detector. The energy throughput is thus higher in a spectrometer using an interferometer than in a conventional machine at the same resolution. It is possible to obtain the same signal to noise ratio (SNR) as a dispersive spectrometer in a significantly shorter time period. The short scanning time of interferometers makes multiple scanning feasible. This also improves the signal to noise ratio which allows for smaller sample sizes. The interferometer has a helium-neon laser which acts as an internal reference for the frequency scale. The calibration of an interferometer can be more accurate and is more stable over the long term than that of a dispersive instrument. Dispersive instruments utilize slits to separate the light into wavelength components. The programs used to control the slits causes the resolution to vary during the scan period. The resolution of an interferometer is constant over all wavelengths. There are no discontinuities in a FT-IR spectrum because there are no grating changes (Perkin-Elmer, 1984).

In addition to being able to measure spectra at high SNR or in a short period of time, the introduction of FT-IR has also led to a much greater variety of forms in which a sample can be presented to the spectrometer through the development of various new sampling accessories. Many of these new devices have been developed in theory for conventional dispersive spectrometers, but could not be used effectively with them because the accessories greatly reduce the energy reaching the detector. These methods include gas chromatography (GC) and high performance liquid chromatography (HPLC)/FT-IR interfaces, infrared microscopy and diffuse reflectance spectroscopy (DR). (Griffiths, 1986).

It was envisaged that this thesis would examine one or more of these techniques applied to the types of samples which frequently occur in art and archaeology. A large number of samples would be run to evaluate the technique for use in a museum or conservation laboratory. The choice of techniques was limited to what was available to the author in terms of instrumentation and also by what seemed to be valid for the types of samples to be analysed. As almost all art and archaeological samples come to the laboratory in the solid form, it was desirable to use a technique

which examines solid samples in the solid state. As the opportunity occurred to use diffuse reflectance, a relatively new technique for powdered solids, it was chosen and extensively used. A FT-IR spectrometer equipped with a microscope was also used and evaluated.

Diffuse reflectance spectroscopy

Development of diffuse reflectance spectroscopy

There are several traditional methods of sample preparation for solid samples for infrared analysis. Each type has certain drawbacks. The best known technique is to grind the sample with an alkali halide such as potassium bromide (KBr) and then to press the sample/alkali halide mixture into a disk by the application of pressure. The problem with the KBr disks is that alterations to the crystal structure of the sample may occur due to the pressure used to produce the disk. Ion exchange between the sample and the potassium and bromide ions has also been observed (Fuller and Griffiths, 1980; Griffiths and Fuller, 1982). It is essential that the sample is well dispersed in the KBr matrix to prevent uneven backgrounds due to scattering and poor line shapes in the sample spectra (Turner and Horres, nd).

Another widely used method is to disperse the powdered sample in mineral oil by forming mulls. All mineral oils have some absorption bands in the infrared and it is usually necessary to measure two spectra using mulling oils which absorb in different regions of the infrared (usually Nujol and Fluorolube). This method is called the split mull technique and the obvious drawback is that it is time consuming (Fuller and Griffiths, 1980; Griffiths and Fuller, 1982).

If the sample is soluble, the material may be examined as a solution. The solvent will affect the spectrum and thus, a solvent should be chosen which has few bands in the infrared. The best solvents are CCl_4 and CS_2 which have few absorptions in the infrared. As with the mineral mulls, two spectra of each sample are required to obtain a complete spectrum of the sample. A further drawback is that many materials are insoluble in CCl_4 and CS_2 (Griffiths and Fuller, 1982).

Polymers may be hot pressed into a film, but such treatment may alter the structure of the material. Films may also be cast from solution if the sample is soluble in a volatile solvent (Fuller

and Griffiths, 1978). It is difficlut to completely remove the solvent from the film.

In an effort to develop a method to analyse solids in powder form, research was pursued into diffuse reflectance spectroscopy (Fuller and Griffiths, 1978; Fuller and Griffiths, 1980; Griffiths and Fuller, 1982). Diffuse reflectance is a widely accepted method for ultraviolet-visible spectroscopy of powders and turbid liquids. It has been applied to clinical measurements, pharmaceutical quality control, heat tranfer studies and food science. It was thought that insufficient radiation would be reflected from a powdered sample to obtain satisfactory infrared spectra (medium resolution, 2-4 cm^{-1}, and high SNR), so diffuse reflectance had not been considered feasible for infrared analysis (Fuller and Griffiths, 1978).

An integrating sphere device is used to collect the diffusely reflected ultraviolet-visible and near infrared radiation. In such a device, the sample and detector are usually positioned at the interior sphere surface which has been coated with a nonabsorbing, diffusing powder such as MgO or $BaSO_4$ (Fuller and Griffiths, 1978).

The integrating sphere could not be directly adapted for measurements in the mid-infrared. Infrared detectors are much less sensitive than the photo-multiplier tubes which are used in ultraviolet-visible spectroscopy. The integrating spheres do not efficiently collect the radiation and the resulting SNR is low. Also, efficient coatings for the sphere interior had not been developed for infrared spectroscopy (Fuller and Griffiths, 1978).

Until 1978, there were few reports of diffuse reflectance spectroscopy in the mid-infrared. Willey (1976) was among the first to interface an integrating sphere to a FT-IR. Long measurement times were needed to achieve spectra of high SNR and at only moderate resolution, however (Fuller and Griffiths, 1978; Krishnan and Ferraro, 1982). Several different experimental designs have been tested and hemiellipsoidal and ellipsoidal collecting mirrors are thought to be the most efficient in collecting and transmitting diffusely reflected radiation to the detector (Fuller and Griffiths, 1978). In 1978, Fuller and Griffiths (1978) published their results using a fairly efficient ellipsoidal collecting mirror interfaced to a rapid scanning FT-IR. They were able to obtain spectra at medium resolution and high SNR using fairly short measurement times.

Quantitative Analysis

Although quantitative analysis was not utilized for this thesis, a short summary of the theory as presented by Fuller and Griffiths (1978; 1980) is included. The Kubelka-Munk theory may be used to describe diffuse reflectance at scattering layers in powdered samples. Scattered radiation can be linked to sample concentration in a similar fashion to that embodied by the Boucher-Beer law in transmission spectroscopy. The Kubelka-Munk equation is written as follows for an "infinitely thick" sample:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \qquad \text{(Equation 2.1)}$$

where R_∞ is the absolute reflectance of the sample layer, s is a scattering coefficient and k is the molar absorption coefficient. An ideal standard for diffuse reflectance has not been determined experimentally. A ratio (Equation 2.2) is created where the single-beam reflectance spectrum of the sample, R_∞' (sample), is divided by the single-beam reflectance spectrum of some nonabsorbing standard, R_∞'(standard).

$$R_\infty' = \frac{R_\infty'(\text{sample})}{R_\infty'(\text{standard})} \qquad \text{(Equation 2.2)}$$

The standard must show high diffuse reflectance through the entire the wavelength region being measured (Fuller and Griffiths, 1978). In practice, R_∞ is then replaced in Equation 2.1 by R_∞'.

A linear relationship is suggested to exist between the molar absorption coefficient, k, and the peak value of $f(R_\infty)$ for each band by the Kubelka-Munk theory. The scattering coefficient, s, must be kept constant. The parameters of particle size and range should be kept as consistent as possible since the scattering coefficient is dependent on these factors. For low concentrations of sample in a matrix of low absorbance, it has been proven that:

$$k = 2.303 \epsilon c \qquad \text{(Equation 2.3)}$$

where ϵ is the molar absorptivity and c is the molar concentration. Thus, Equation 2.1 can be rewritten as:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{c}{k'} \qquad \text{(Equation 2.4)}$$

where k' is equal to s/2.303 .

The authors (Fuller and Griffiths, 1978) conclude that "diffuse reflectance spectra of samples dispersed in finely powdered KBr or KCl might be expected to be quite similar to the absorbance spectra of the same samples prepared as a KBr disk." Spectra of cholic acid and carbazole were presented in which this was observed to be true (Fuller and Griffiths, 1978).

The relationship between SNR and sample concentration in the limit of low concentration is somewhat different in diffuse reflectance spectroscopy than in transmission spectroscopy (Fuller and Griffiths, 1980). The Beer-Lambert Law describes the relationship between concentration and transmittance,

$$-\log_{10} T = abc \qquad \text{(Equation 2.5)}$$

where T is the transmittance, a is the absorptivity, and b is the path length. The equation may be written as:

$$T = 10^{-abc} = e^{-2.303abc}$$

$$= 1 - 2.303abc + 2.651a^2b^2c^2 \qquad \text{(Equation 2.6)}$$

The signal of the absorbing sample, 1 - T, is given as the limit as 2.303abc as c tends to zero. Thus, the SNR has a linear relationship to c at low concentrations. The Kubelka-Munk equation describes the relationship for diffuse reflectance for

"infinitely deep" samples (Equation 2.4) which can be written as follows:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{2.303ac}{s} \qquad \text{(Equation 2.7)}$$

where s represents the scattering coefficient and R_∞ is the ratio of the diffuse reflectance of the dilute sample "at infinite depth" to that of the nonabsorbing matrix alone. R_∞ approaches unity as the sample concentration within the non-absorbing matrix is decreased, Thus:

$$(1 - R_\infty) = \left(\frac{4.605ac}{s}\right)^{1/2} \qquad \text{(Equation 2.8)}$$

and the SNR becomes proportional to the square root of the sample concentration. This phenomenon is thought to be unique to diffuse reflectance spectroscopy and is an obvious improvement in the analysis of very small samples (Fuller and Griffiths, 1980).

The diffuse reflectance of powdered gold, germanium and some alkali halides was measured in an attempt to select a suitable material for the nonabsorbing background (Fuller and Griffiths, 1978). Powdered KCl was found to exhibit the highest reflectance with the least interferences. The particle size of KCl was found

to affect the reflectance. The smallest average particle size was observed to give the highest reflectance at high wavenumbers. A standard dispersing matrix of KCl at a particle size less than 10 μm has been recommended (Fuller and Griffiths, 1978).

It is important to note that the Kubelka-Munk equation is only valid for moderately absorbing materials having a limited particle size range (Fuller and Griffiths, 1978). A "Kubelka-Munk law" plot of $f(R_\infty)$ versus weight percent of sample becomes non-linear at high sample concentrations. Particle size affects both bandwidths and relative intensities. A decrease in particle diameter is observed to reduce bandwidths significantly. Variation in particle size has been observed to affect the intensity of certain bands to a greater extent than others (Fuller and Griffiths, 1978).

It is necessary to keep particle size constant when comparing diffuse reflectance spectra of a series of similar substances. It is vital that pure alkali halide powder should be used for diffuse reflectance, especially for microsampling. The same stock of alkali halide should be used for comparison of related compounds (Krishnan and Ferraro, 1982).

Experiments suggest (Fuller and Griffiths, 1978) that spectral subtractions of diffuse reflectance spectra are valid if the $f(R_\infty)$ is low for both spectral components. Attempts to subtract the entire spectrum of one sample from another which were not diluted with KCl were not successful. A later reference indicates that diffuse reflectance can be used quantitatively only over narrow concentration ranges (Krishnan and Ferraro, 1982). Quantitative results have been reported (Turner and Horres, nd) using a Bruker FT-IR spectrometer with a Harrick "praying mantis" type diffuse reflectance unit. In the study, spectra were obtained of finely ground ascorbic acid at concentrations of 1, 2, 4 and 8% in KBr. The peak heights of four bands were plotted against concentration. A nonlinear relationship was observed for the raw data and linear plots were found for data corrected by the Kubelka-Munk equation which is in agreement with the results of Fuller and Griffiths (1978).

Particle size and concentration are not the only factors which affect the spectrum by causing deviations from the theoretical Kubelka-Munk situation. There is a specularly reflected component in the radiation that is sent to the detector that is caused by the radiation which bounces off the surface of the

sample without penetrating into the sample. For specular or regular reflectance, the angle of incidence is equal to the angle of reflectance. In diffuse reflectance, the direction of reflected light is random with respect to the incoming beam (angle of incidence) (Figure 2.2)(Willey, 1976). Diffuse transmittance and regular transmittance have a similar relationship to diffuse and regular reflectance. For diffuse reflectance, the depth of penetration is a function of the internal scattering of the material. The total reflectance spectrum is due to the reflection from the surface plus the scattering and absorption of the particles in the medium (Willey, 1976).

The specular reflectance for most organic compounds from a single crystal is very small at all wavelengths. This is attributed to the relatively small absorptivity of the absorption bands which leads to only small changes in the refractive index across the spectrum (Griffiths and Fuller, 1982).

Specular reflectance is a concern for many inorganic compounds, the absorptivity of the stronger bands can be very large and the refractive index can change dramatically across the band. This

is called anomalous dispersion which leads to the appearance of spurious reststrahlen bands in the specular reflectance spectrum. If small, irregular crystallites are examined instead of a single crystal, the resulting spectrum contains a combination of diffuse and specular reflectance. The larger the absorptivity of a particular band and the larger the crystal, the more closely the spectrum will resemble the specular reflectance spectrum. The specular component decreases and the diffuse reflectance radiation increases as particle size decreases. However, there is still an element of specularly reflected radiation which does not penetrate into the bulk of the sample, but instead reflects off of the particles on the top layer of the sample. Band inversion or when a negative absorption appears above the baseline may occur in the region of intense bands in the spectrum. When inorganic samples are ground with an inert, nonabsorbing matrix such as KCl, the diffuse reflectance spectrum more closely resembles the typical absorption spectrum. If quantitative information on minerals is to be obtained with diffuse reflectance, the sample should be ground with KCl in a concentration of 1% (Griffiths and Fuller, 1982).

Qualitative analysis

Diffuse reflectance is a powerful qualitative technique for rapid identification of powdered solid samples with little or no sample preparation (Fuller and Griffiths, 1978). The amount of sample needed is very small. A strong spectrum may be obtained from only 100 μg of sample in most cases and as little as 200 ng of sample is sufficient to record a spectrum for moderately absorbing substances. A spectrum has been observed from 2 ng of sample in KCl in a few rare cases. A matrix thickness of less than 5 mm is reported to be the point where a further increasing thickness does not change the spectrum, ie "infinite thickness". There seems to be very little difference in band intensity between sample thicknesses of 2 to 5 mm (Fuller and Griffiths, 1978).

The microsampling capabilities of diffuse reflectance were compared to those of transmission spectroscopy using KCl disks. Two mixtures of carbazole and KCl were prepared, one with a carbazole concentration of 0.37% and one with a concentration of 53 ppm. KCl disks were prepared from both mixtures and transmission spectra were obtained of each disk. Diffuse reflectance spectra were obtained of both concentrations without any further sample preparation. All of the major bands appear in

both the transmission spectrum of the KCl disk and the diffuse reflectance spectrum of the 0.37% mixture. A clear diffuse reflectance spectrum was also obtained of the very dilute mixture. Only the strongest bands, however, appear in the transmission spectrum of the KCl disk of the 53 ppm concentration. The spectra were collected under identical instrumental conditions. The band intensity of the diffuse reflectance spectrum of the 53 ppm concentration is about one order of magnitude greater than in the transmission spectrum of the KCl disk of the same concentration (Fuller and Griffiths, 1980). The detection limits were further investigated by recording the spectra of mixtures of a given amount of KCl with 11 μg, 250 ng and 11 ng of caffeine (1000 scans and 4 min scanning time). The stronger absorption bands are easily seen above the noise level in the spectrum of the 11 ng sample (Fuller and Griffiths, 1980).

One microsampling problem with infrared spectroscopy is measuring solutes at low concentration. The traditional method requires that the concentration of the solute is first increased either by evaporation of the solvent or by extraction of the solute into a smaller volume of an immiscible solvent. A small amount of KBr

is added and the residual solvent is removed by boiling away or freeze-drying. The sample remains on the surface of the KBr and the material is then pressed into a micropellet. The diffuse reflectance spectrum could instead be obtained from the unpressed powder sample. The above procedure has been automated and utilized in the interface between a HPLC and a diffuse reflectance spectrometer (Fuller and Griffiths, 1980). The detection limits for such measurements are very low (approximately 100 ng). The intensity of the bands of a 1% sample of carbazole deposited on the KCl from solution was observed to be greater than those from a spectrum of finely ground carbazole mixed with powdered KCl at a concentration of 1% (Fuller and Griffiths, 1980).

The relative intensities of analyte mixed with KBr are different from those for the sample pressed into a KBr disk. The effect is particularly noticeable in aromatic compounds when the relative intensities of bands in the overtone region 1700 - 2000 cm^{-1} and the fundamental modes are compared. The overtone bands are condiderably stronger in the diffuse reflectance spectrum. However, the relative intensities in the diffuse reflectance spectrum of the samples prepared by depositing the analyte from

the solution onto the KBr powder seem to be much more similar to those observed in the transmission spectrum of the KBr pellet (Fuller and Griffiths, 1980). " This effect is thought to be due to the small thickness of the solute film on the KCl particles relative to the wavelength of the infrared radiation when the analyte is deposited from solution as opposed to the comparatively large particle diameter of the sample when mixed with the KCl." However, no thoery was presented describing the reasons for this phenomenon (Fuller and Griffiths, 1980).

Diffuse reflectance is an easy way to measure infrared spectra of solids and obtain high quality results. It is particularly effective for materials such as coal and minerals that are difficult to study as alkali halide pellets. It is hard to grind such materials into the fine uniform powders which are needed to produce pellets without scattering effects (Krishnan and Ferraro, 1982). The sample preparation time is reduced, the complete spectrum can be measured and the chance of ion exchange is lessened. It is possible to obtain spectra of neat samples, but it is preferable to grind organic samples in approximately twenty times their weight of KCl for one to three minutes. Inorganic

samples need to be mixed with more alkali halide to yield an acceptable spectrum (Fuller and Griffiths, 1980).

There are some problems which are associated with the use of alkali halides as reference materials for diffuse reflectance. Alkali halides tend to adsorb water which causes bands at 3300 and 1640 cm^{-1}. It also adsorbs organic materials from the air if it is left in a powdered state for several hours. Thus, the alkali halide material should be stored as lumps and ground as needed shortly before use (Griffiths and Fuller, 1982). Other materials were examined to see if they could be used to replace alkali halides. Silicon and germanium were tested because of their purity and ease of grinding. When the ratio of a spectrum of KCl to that of finely ground silicon or germanium was calculated, absorption bands indicating water (3300 and 1640 cm^{-1}) and organics (2950 cm^{-1}) appeared. Unfortunately, silicon and germanium exhibit strong bands at 1100 and 900 cm^{-1} respectively which are thought to be due to oxide layers on the powder surface. Also, the overall reflectance of these materials is substantionally less than that of KCl. When a ratio of a diffuse reflectance spectrum of an organic compound in silicon or germanium to that of silicon or germanium was calculated, the

baseline was often found to be above 100% which causes difficulty with quantitative work (Griffiths and Fuller, 1982).

Silicon carbide paper sampling technique

A new method of collecting powdered material for infrared analysis has been suggested (Sharp, 1982; Jansen, 1983) where silicon carbide abrasive paper is used to grind the sample. The first report (Sharp, 1982) recommended the use of "wet and dry" paper. Three drops of deionized water are placed on a small piece of silicon carbide paper. The sample is rubbed onto the paper until a fine suspension of sample is collected in the water. The sample suspension is rinsed with 1-2 cm^3 water into a centrifuge tube and centrifuged for one minute. After decanting the water, the material is added to 0.7 g KBr, mixed, gently dried and then it is ground and pressed into a pellet. If the object is large or cannot be sampled in the lab, its surface may be moistened and rubbed with the wet and dry paper (Sharp, 1982). Another report (Jansen, 1983) suggests that the sample and the KBr be ground together with a pestle on the abrasive paper. Water is not used and the resulting mix is then pressed into a pellet. Dichloroethane is recommended for use with rubber materials. The author points out that the use of silicon carbide

paper allows a small amount of sample to be removed at positions where little or no harm is done to the appearance or function of the object. The technique is also useful for objects which cannot be destroyed (Jansen, 1983).

A further refinement of the silicon carbide technique occurred when it was suggested that the diffuse reflectance spectrum could be measured directly from the surface of the powder *in situ* on the silicon carbide paper (Spragg, 1984; Perkin Elmer, 1986). The technique is suggested for materials which may be difficult and time consuming to grind instead of using a vibration mill or mortar and pestle. The sample is rubbed onto the paper until sufficient sample has been accumulated and the spectrum is measured directly from the paper. The preparation time is very short, usually only a few seconds and very little sample is needed. It has been mentioned before that diffuse reflectance spectra are most similar to transmission spectra when the samples are mixed with a nonabsorbing matrix. When neat samples are measured, the relative band intensities and band shapes may vary considerably from those in a transmission spectrum. The spectra are however, often adequate for qualitative indentification or quality control (Spragg, 1984).

There does not seem to be much if any, spectral interference from the silicon carbide paper. A spectrum can be obtained by calculating the ratio of the spectrum of the paper against the spectrum of the plane mirror (Perkin-Elmer, 1986). A spectrum was obtained of the silicon carbide paper used in this thesis and is reproduced in Shearer, 1987. A number of different silicon carbide papers were tried and 200 grit was found to be satisfactory for a variety of materials (Spragg, 1984; Perkin-Elmer, 1986). In some types of paper, the spectra only exhibited a silicon carbide reflectance peak near 800 cm^{-1} and very little evidence of other materials such as organic adhesives. In the spectra of other examples, the presence of organic binders is stronger. The spectrum of English Abrasives paper "p220C" contains many weak bands due to organic components, but the peak at 800 cm^{-1} is less intense than in the spectra of most other examples of silicon carbide paper (Spragg, 1984). There is a considerable difference in the intensity of the background spectra of various papers. A variety of examples from different sources should be examined to minimize the possible interferences. Very stiff paper provides ease of handling.

Spectra were measured of a plastic moulding material which was identified as an acrylonitrile-butadiene-styrene copolymer (Spragg, 1984). A diffuse reflectance sample was prepared by abrasion of the material by silicon carbide coated paper. The spectrum of the powdered sample on the surface of the paper was measured. The amount of sample on the paper was 150 μg on an area of 35 mm^2. The spectrum was compared to that of a film cast from a solution of 1,2-dichloroethane on a KBr window. The spectra were collected at a resolution of 5 cm^{-1} and one scan was collected. There are no features in the diffuse reflectance spectrum which can be attributed to the silicon carbide paper. The bands observed in the diffuse reflectance spectrum correspond very closely with those in the transmission spectrum of the cast film (Spragg, 1984). The relative intensities of the corresponding bands are very similar. The similarity between the transmission spectrum and the diffuse reflectance spectrum is thought to be due to the sample being thinly distributed on the silicon carbide paper. The infrared radiation still has to travel different path lengths, but they are all fairly short (Perkin-Elmer, 1986) Thus, the silicon carbide paper has a similar effect to diluting the sample in a nonabsorbing matrix.

This observation agrees with that of Griffiths (1986) who states that diffuse reflectance spectroscopy is most successful when the sample is in the form of a very thin layer on the surface of a diffusely reflecting support.

The sample loading or amount on the paper does not need to be closely contolled for qualitative spectroscopy. The sample in the above illustration was obtained from sample loading of approximately 5 $\mu g/mm^2$. At this concentration, most of the sample is trapped within the crevices of the surface and the silicon carbide is still visible. (Spragg, 1984). The reflectance at this level is 1 - 2% in contrast to approximately 10% for finely powdered KBr in the diffuse reflectance accessory. The reflectance can be increased by adding more powdered sample (Perkin-Elmer, 1986). The reflectance in the areas where the sample does not absorb increases by as much as a factor of 2 (Spragg, 1984). However, the contrast between weak and strong bands is reduced (Spragg, 1984; Perkin-Elmer, 1986). An effect similar to measuring the diffuse reflectance of a neat powdered sample is achieved. The reflectance can also increase by rubbing the silicon carbide paper with powdered KBr although this

somewhat reduces the convenience of the method (Perkin-Elmer, 1986).

In the diffuse reflectance accessory used in the experiment (Spragg, 1984), the infrared beam is focussed down to an area approximately of 2 mm^2. When the sample is collected by being rubbed on the surface of the silicon carbide paper, it will be distributed over a larger area than is needed. The amount of sample taken can be reduced by cutting a piece of silicon carbide paper to the appropriate size and rubbing the smaller piece on the surface of the bulk sample. The sample size taken can be reduced to 20 ug or less (Spragg, 1984).

The silicon carbide sampling technique is fast and convenient. It is useful for polymeric materials which are difficult to grind and is appropriate for large objects (Spragg, 1984). The least success was obtained with very soft materials and substances which are torn into particles which are too large for direct measurement by diffuse reflectance spectroscopy.

The use of the silicon carbide technique is also mentioned in an article on industrial applications of diffuse reflectance FT-IR spectroscopy (Chalmers and Mackenzie, 1985). It was suggested

for use with materials which were difficult to prepare by other more conventional techniques. Examples included poly (aryl ether sulphone)(PES) which is a high temperature thermoplastic which is difficult to compression mould into a film which is sufficiently thin to obtain a satisfactory spectrum. It is also difficult to remove the last traces of solvent from a cast film of the material. Another example cited was surface analysis of corrugated glass-reinforced plastic sheeting which does not form good contact with the reflection element for MIR (multiple internal reflectance) analysis. The silicon carbide paper was also used for identification of minerals. It was recommened that the surface of the silicon carbide paper should be dusted with KBr when analyzing inorganic materials. Although the technique is primarily of qualitative interest, it was suggested that it would be useful in industrial situations (Chalmers and Mackenzie, 1985).

Other applications of diffuse reflectance spectroscopy

It has been found that sufficient SNR can be obtained with a Harrick praying mantis type accessory linked to a high performance Perkin-Elmer model 983 conventional dispersive spectrometer and lower performance machines such as the Perkin-

Elmer model 1430 conventional dispersive spectrometers (Hannah and Anacreon, 1983). The silicon carbide paper technique was originally developed using a diffuse reflectance accessory and a conventional dispersive infrared spectrometer (Spragg, 1984).

A diffuse reflectance accessory has been designed to allow in situ analysis of a small surface area of large objects without the need to take samples (Korte and Otto, 1988). The design requirements included that the specularly reflected radiation component be directed away from the detector and that the optical energy throughput be high enough to obtain satisfactory spectra. A large portion of the reflected radiation from samples with smooth surfaces such as varnishes and coatings is due to specular reflection. The authors concluded that the reflectance for compact samples is low when compared to that of powdered samples in an alkali halide powder matrix. The diffuse reflectance spectra of different thicknesses of an acrylate/isocyanate varnish with metallic flake pigment were found to fairly closely resemble the absorbance spectrum of the material. However, samples of a weakly scattering polyester varnish gave a low reflectance, although it was possible to measure spectra. There are, however, significant variations in the relative band

intensities between spectra of various thicknesses and in comparison to the transmittance spectrum of the material. The location of certain strong bands has also been observed to shift to higher wavenumbers. The authors concluded that the distortions are caused by Fresnel reflection (specular reflectance component) and that the device does not reject all of the specularly reflected radiation. When samples of low reflectance are analysed, it is necessary to obtain as high an energy throughput as possible. In this system however, higher energy throughput would result in a greater specular reflectance component in the total radiation. It was concluded that varnishes and coatings are not idealy suited for diffuse reflectance spectroscopy, but that acceptable spectra could be measured in moderate scanning times with no removal of sample (Korte and Otto, 1988). This technique is obviously ideal for extremely valuable objects which cannot be sampled, but if a very small amount of sample may be taken, it is possible to obtain higher energy throughput without severe specular reflectance.

Multicomponent analysis

Introduction

One drawback of the diffuse reflectance method is that it produces a spectrum of the total sample and it is difficult to distinguish several substances, especially if the materials are similar chemically. The obvious solution is spectral subtraction, although this is difficult with diffuse reflectance measurements that are not strictly controlled for quantitative analysis. It is of limited validity with the silicon carbide method. Three possible alternatives will also be discussed: thin layer chromatography (TLC) for separation of sample components before FT-IR analysis, the infrared microscope and high performance liquid chromatography-FT-IR interface.

Thin layer chromatography/FT-IR

Early attempts to measure the infrared spectra of materials separated by thin layer chromatography directly from the spots on the TLC plates using emission spectroscopy, specular reflectance and ATR spectroscopy were not successful. A technique was developed where the spot could be analysed in situ on the plate without eluting the sample spot by transmission spectroscopy. The plates used were composed of silver chloride with a thin

layer of silica gel or alumina. The thickness of the adsorbent was kept as thin as possible and the interferences from the silica gel and the alumina were removed by using the ratio of the sample spectrum to a spectrum of the plate (Percival and Griffiths, 1975). The method was successful, but the adsorbent caused scattering at high frequencies which reduced the signal to noise ratio. It was found that treatment of the plate after development with a substance whose refractive index approximately matches that of the adsorbent such as Nujol or Fluorolube improved the sensitivity of the method in the higher wavelength regions (Gomez-Taylor et al., 1976). The sensitivity of the method was further increased by the use of programmed multiple development which reduced the sample spot size which increased the chromatographic resolution and the utilization of a MCT detector which decreased the sample scanning time needed (Gomez-Taylor and Griffiths, 1977).

It was suggested that since the strong bands of an adsorbed species can be detected in strongly absorbing matrices such as silica gel, that it should be possible to obtain spectra of components separated by TLC without sample preparation. A spectrum of 1.2 μg of methylene blue on a silica gel plate was

obtained (Fuller and Griffiths, 1978), however, further research by the same workers was not successful (Fuller and Griffiths, 1980). The spectrum of the adsorbent must be either subtracted or used to obtained a ratio in order to record a satisfactory spectrum of the adsorbate (Griffiths and Fuller, 1982). The absorptivity of silica gel is much higher than that of charcoal or XE-340 graphitized polymer beads in several diagnostic areas of the spectrum. Also, it is very difficult to see the bands resulting from the adsorbates due to the high attenuation of the beam in the region of the silica absorption bands. It was also observed that the exposure of the silica gel to a solvent tends to change its surface and cause small shifts in frequency and intensity changes. This results in a very uneven background in the ratio spectrum. The choice of reference material is vital in order to obtain an adequate spectrum (Fuller and Griffiths, 1980). It does not seem to be possible to adequately compensate for the very strong bands due to the adsorbent (Griffiths and Fuller, 1982).

Fuller and Griffiths (1980) concluded that better results were observed when the sample was extracted from the silica gel before the spectrum was measured. Each spot was scraped off the support

and extracted with about 0.5 ml of acetone. The slurry was stirred and centrifuged for one minute. The solvent was then decanted, evaporated in air to 150 µl and deposited onto a sample cup packed with KCl. The diffuse reflectance spectrum was then obtained from the powder after the residual solvent had evaporated. It was also found that some silica gel remained suspended in the solution and intense silica bands could be observed in the spectrum. The residual silica gel was removed by passing the supernatent liquid through a sintered glass filter after centrifuging. It was also concluded that there is a high degree of susceptibility to interferences due to the very high sensitivity of diffuse reflectance microsampling. One has to be very careful during sample preparation and spectral interpretation when the sample amounts being measured are near the detection limit of the technique (Fuller and Griffiths, 1980). The same conclusions on measuring the spectra of TLC spots *in situ* were reached by other workers (Chalmers and Mackenzie, 1985).

HPLC/FT-IR

The interface between HPLC or GC and diffuse reflectance FT-IR seems to be a more promising method for examining multicomponent

systems. These techniques were not available for this research, but a certain amount of work has been published on the subject. Gas chromatographs (GC) have also been interfaced with FT-IR spectrometers for on-line measurements of infrared spectra of peaks as they elute from the GC colum. The sensitivity of the systems are now high enough to recommend an FT-IR spectroscopy interface as an alternative or complement to a mass spectrometer interface for qualitative analysis of multicomponent mixtures which are sufficiently volatile and thermally stable to be separated by GC. HPLC is usually used to separate nonvolatile or thermally labile components. However, the interface between HPLC and FT-IR is more difficult than for GC and FT-IR. The detection limits of an early commercial model were greater than those of equivalent GC/FT-IR systems (Kuehl and Griffiths, 1980).

The difficulty with sensitivity in HPLC/FT-IR systems is caused by the strong infrared absorption of the mobile phase. In conventional systems, the effluent passes through a flow cell and the spectrum of each HPLC peak is recorded and stored during the chromatographic run. After the chromatogram has run, the solution spectra are computed and the solvent bands are removed by subtraction. It is necessary to keep the pathlength of the

flow-cell very small to prevent the solvent absorption bands from "blacking out" very large regions of the spectrum. The recommended pathlength for most solvents used for normal phase HPLC is about 100 μm. The volume of 3 mm diameter cells is less than 1 ul and less than 1% of each sample is present in the cell at any time during the collection of the solute spectrum. This severely limits the sensitivity of the system (Kuehl and Griffiths, 1980). Kuehl and Griffiths (1980) describe a system where the effluent from the column is concentrated and deposited onto KCl powder. The residual solvent is removed by rapid evaporation and the solute remains on the KCl. The diffuse reflectance spectrum of each fraction is then measured.

The detection limits of the system are determined by chemical interferences and not by the noise level of the instrument. Solvent which has not been evaporated can cause interferences depending the nature of the solvent. The best results are obtained with highly volatile, fairly nonpolar solvents. A second problem is atmospheric moisture which can become adsorbed to the KCl powder. The water can usually be removed by treating a reference cup of KCl in the same manner as the samples, but on humid days or when very large ordinate expansion is needed, bands

due to water are sometimes seen in the spectra. Only very pure KCl should be used. Since diffuse reflectance spectroscopy results in much more intense bands than conventional transmission measurements, it is essential to minimize comtaminants from all sources in order to obtain low detection limits (Kuehl and Griffiths, 1980).

There are several disadvantages to the HPLC/diffuse reflectance system. The solutes must be much less volatile than the solvent. This is not a serious limitation as most volatile samples are analysed by GC. The second difficulty is that water cannot be completely eliminated because of its high surface tension and latent heat of evaporation. This limits the application of FT-IR to size exclusion or normal phase HPLC. Systems which require an aqueous phase cannot be used in conjunction with FT-IR because of the strong absorption bands due to water. The third and most serious problem is due to the fact that in this system, the detector signal of the HPLC acts as a trigger mechanism for the recording of an FT-IR spectrum so the solute must be detected by the detector for the system to work. The authors discuss the possiblity of a fully automated system (Kuehl and Griffiths, 1980).

The HPLC/FTIR system has another advantage which is of interest with archaeological samples or other samples of limited availability. Each component is collected into sample cups and not destroyed. If the spectrum obtained by the on-line method is unsatisfactory, the sample can be re-run with the signal averaged over a longer period of time to improve the SNR or it may be recovered from the KCl with a nonaqueous solvent and analysed by a different technique (Kuehl and Griffiths, 1980).

The use of HPLC with diffuse reflectance FT-IR is mentioned by other workers (Chalmers and Mackenzie, 1985). In their paper, the separation was carried out using reverse phase chromatography with a water/methanol mobile phase and the separated fractions were collected into vials. The aqueous solvent was evaporated using a steam bath and the solute was redissolved in a minimum quantity of dichloroethane and deposited by a capillary pipette onto powdered KCl. Satisfactory spectra were obtained of 20 and 2 ug quantities of sample (Chalmers and Mackenzie, 1985).

Until the development of the diffuse reflectance FT-IR system, FT-IR instruments had not been sufficiently sensitive to identify minor constituents of mixtures separated by adsorption

chromatography due to problems with the mobile phase (Kuehl and Griffiths, 1980). However, one technique in which the solvent does not need to be removed before infrared measurement of each fraction is size exclusion chromatography where the choice of solvent does not seriously alter the separation. Solvents with good infrared transmittance such as CCl_4 and CS_2 may thus be used as the mobile phase for size exclusion chromatography. However, these solvents are not completely transparent in the infrared and spectral subtraction techniques are not yet sophisticated enough to remove all solvent bands when gradient elution is required for chromatographic separation (Kuehl and Griffiths, 1980).

FT-IR microscopy

Although microscope accessories have only been widely available since 1983, the idea is not new and the model introduced by Cole and Jones shows similarities to the microscopes which are now available (Griffiths, 1986). A microscope interfaced to a ultraviolet-visible spectrometer and a quartz refracting instrument was used to measure spectra in the ultraviolet region. However, the instrument had to be refocused as the wavelength changed and the system of lenses absorbed in certain regions which limited the range which could be examined (Barer et al.,

1949). In 1947, Burch developed a reflecting microscope which was achromatic and no absorbing materials were used in the construction. The instrument was applicable to spectrometry from the ultraviolet to the infrared regions. The Burch microscope was attached to a Perkin-Elmer infrared spectrometer by Barer et al. (1949) and spectra of particles were obtained from 2 to 15 um without the need for large slit widths which would severely reduce the the spectral resolution. The instrument was fitted with sodium chloride and lithium fluoride prisms, and the radiation from a Nernst glower source was passed through the microscope and sample. The image was magnified 100 - 1000 times. The sample was held on a thin plate of rock salt, quartz or other infrared transparent material. A small, adjustable preliminary slit was used to select the area to be analysed and the radiation was directed by focusing mirrors through the sample area selected onto the entrance slit of the spectrometer. The sample size used was 10^{-7} - 10^{-8} g. The minimum sample size was controlled by the resolving power of the microscope which varied with the wavelength. Results were obtained with crystals and fibres which were 20 - 50 um in diameter. Polarization effects were studied with a selenium mirror (Barer et al., 1949).

The experiment was repeated by Gore (1949). A Bausch and Lomb Grey design Type IV microscope was interfaced to a Perkin-Elmer Model 12B infrared spectrometer. The microscope was equipped with a 0.4 numerical aperture condenser and objectives and only reflecting elements were used. An auxillary source was used to collect the radiation and direct it to the condensing system. After the radiation passed through the sample, it was collected by the objective and directed through a draw tube. The radiation was then collected by a spherical mirror in the spectrometer which directed the magnified image onto the entrance slit. The diameter of the image was made equal to the length of the slit by adjusting the physical dimensions of the slit. The size of the image could also be controlled by adjustment of the sample on the microscope stage. The suggested sample preparation methods included suspension of specimen in mineral oil on a NaCl plate or between two plates. The material may also be placed in solution or attached to a stretched fine wire. The sample size used was estimated to be 0.3 μg at 4000 cm^{-1} to 3.0 μg at 650 cm^{-1}. The black body characteristics of the energy source required that the slit width be increased as the wavelength increased. Macro and micro sample spectra were obtained of sodium benzyl penicillin

and it can be seen that the wide slit widths needed adversely affect the resolution near 2400 and 1325 cm^{-1} (Gore, 1949).

Coates et al. (1953) introduced a modified design for an infrared microscope interfaced to a Perkin-Elmer single beam spectrometer. In this design, the microscope is mounted so that the radiation passes from the exit slit of the monochromator to the microscope and then to the detector. This inovation decreased the possible damage to the sample from the heat and photochemical reactions. The condenser and objective pair were of the Schwarzschild type and the numerical aperture is 0.75 and the obscuration ratio is 0.4. Accurate selection and measurement of sample area is provided by a viewing and manipulation system. Approximately 35% of the radiation from the monochromator is passed through the microscope system by minimizing the number of reflecting surfaces. Field mirrors were used to provide more efficient transfer of energy. The radiation is measured by a separate detector and preamplifier which were subsequently connected to the system amplifier and recorder. The minimum sample size was dependent on the wavelength and limited by the energy available. The system was used to provide spectra of fibres, crystals, biological tissues and small volumes of solution in cells (Coates

et al., 1953). The system was marketed under the name Perkin-Elmer model 85, but it was not a commericial success with only limited production (Reffner et al., 1987).

The introduction of computers facilitated the growth of microspectroscopy. In 1980, V. Coates and his firm (Nanometrics) introduced the NanoSpec 20IR which consists of a single beam monochromator instrument, a computer and an infrared microscope. The computer facilities are used to generate a double beam format spectrum from the single beam sample spectrum and a background spectrum which is stored in its memory. The resulting spectrum does not contain absorptions due to the atmosphere or instrument background which appear in conventional single beam spectra. The scanning time needed for this instrument is two minutes or less. The use of FT-IR spectrometers also promoted the growth of microspectroscopy. The advantages over conventional dispersive spectrometers provided by FT-IR also apply to the use of the microscope. These include high energy throughput, good spectral resolution, high signal to noise ratio, rapid data collection and digital processing of spectral data. The interface was first demonstrated in 1982 by McCrone Associates (Reffner et al., 1987) and in 1983, Digilab introduced the first commercial microscope

accessory for FT-IR (Griffiths, 1986) and Analect also produced a version that year (Reffner et al., 1987). Microscope accessories can now be obtained for all FT-IR spectrometers (Reffner et al., 1987). The Digilab model was originally only able to measure transmission spectra. It was later updated to perform reflectance measurements as well. There are two types of microscope accessory available. The most expensive high performance microscope systems are equipped with their own mercury cadmium tellurium MCT detector. The less expensive models use the MCT detector within the spectrometer (Griffiths, 1986).

When utilizing infrared microscopy, the sample to be analysed usually covers a much smaller dimensional area than the total area of the instrument light beam which is projected onto the sample plane of the microscope. The dimensions of the radiation must be decreased to match those of the sample. This is usually accomplished with four moveable slit edges located at an auxiliary light focus. The result is that the image of the sample covers only a small part of the area of the detector. The detector is optimized to take advantage of the superior throughput and the SNR can be significantly increased by the use

of a MCT detector which has been optimized for the microscope. Reasonable spectra can be obtained from a sample of 20 um square with a scanning time of a few minutes. Smaller samples present a difficult problem as the sample size is then equal to or smaller than the wavelengths of the light being used. The diffracted light will bypass the sample if the beam is blocked in some way by slit edges at an auxiliary focus. One solution is to mount the sample on a pin-hole in an opaque plate in the sample plane, but care must be taken that the plate is thin to avoid obscuring the beam (Griffiths, 1986).

The thickness of the sample is important to obtain satifactory transmission spectra. The sample thickness should be of the correct magnitude, between 5 and 50 μm, to yield an acceptible spectrum. For specimens which are too thick, the material can be squeezed between two type II diamonds. This reduces the thickness and increases the cross-sectional area of the sample. A larger quantity of the radiation is then able to pass through the sample since there is more open area. Thus, the SNR and the quality of the resulting spectrum are increased. This technique is thought to be more successful than mounting the sample behind a pin-hole (Griffiths, 1986).

A microscope has been developed by Spectra-Tech which combines high quality visual imaging with the reflecting optics necessary for infrared measuring. The other available infrared microscopes do not have the capability to perform high quality research light microscopy. The accessory is known as the IR-PLAN has both transmission and reflection capabilities so spectra may be measured through the sample and by reflection of the surface. The visual light path is coaxial with the infrared light path so the image selected is the same that is analysed. The sample area is defined and stray light is reduced by remote variable apertures which are located at conjugate image planes. This technique is refered to as redundant aperturing (Spectra-Tech)(Reffner et al., 1987).

There is a very wide variety of uses for the infrared microscope and the advantages for archaeological and art samples are obvious. The microscope can be used for cross-sectional analysis. It is useful for identifying components in layers without chemical separation or "peeling" of layers which is difficult and often incomplete. An example was given of analysis of a plastic laminate. A thin cross-section was prepared by microtomy and infrared analysis of each layer including the

adhesives was obtained after each material was optically isolated with the dual remote variable apertures. The separation achieved with the redundant aperturing technique seems to be very efficient. The report did not indicate the support used for the cross-section (Reffner et al., 1987).

The microscope in reflecting mode may be used to analyse surfaces in situ. The method is similar to reflection accessories used with FT-IR. The method can be nondestructive with no sample preparation but the sample geometry must be correct. The object may be analysed either directly on the stage where the size of the sample is limited by its space available between the objective and the stand or using a sideways facing external objective port. This may be used to examine large or bulky samples. The reflection microscopy method is best suited for studies of surface coatings and contaminant films (Reffner et al., 1987).

Another sampling advantage of infrared microscopy is found with the identification of fibres. In the past, the identification of monofilament fibres was difficult with infrared spectroscopy due to band distortions caused by diffraction effects. This problem

is overcome by the remote aperturing system. Also, bicomponent systems can be studied. The light imaging facilities can be used to measure the morphology and optical properties to distinguish the sample from other fibres. Conventional infrared sample preparation techniques cannot be used to identify the microstructure of bicomponent fibres. Techniques such as grinding the material into KBr pellets, dissolving and casting it into films or infrared reflection destroy the microstructure of the fibre. Both microscopy and spectroscopy are thus desirable for complete characterization (Reffner et al., 1987).

Another advantage of the microscope is the ability to characterize solid mixture system without physical separation or bulk analysis of all components. The sample can be separated into its components by differences in crystallinity or morphology. The crystals may be differentiated by shape or birefringence using cross polarized light. If the crystal is too large, it is necessary to crush it to obtain a sample of the optimum size (Reffner et al., 1987).

Figure 2.1 Diagram of the Michelson interferometer (Griffiths and de Haseth, 1986). (F) is the fixed mirror, (M) is the moveable mirror, (B) is the beamsplitter, (S) is the source and (D) is the detector.

Figure 2.2 Illustration of specular and diffuse reflectance (Willey, 1976).

CHAPTER 3 EXPERIMENTAL PROCEDURE

Instrument Specifications

FT-IR Spectrometers

The diffuse reflectance measurements were carried out using a Perkin-Elmer 1710 infrared Fourier transform spectrometer. The machine design is an improved single beam Michelson interferometer with rotary scan and bi-directional data collection (Perkin-Elmer, 1984).

The optical unit, which contains a Michelson interferometer system similar to that described in Chapter 2, is sealed and filled with molecular sieve dessicant to reduce absorptions due to atmospheric contaminants. The beam splitter is coated with germanium and a variable Jacquinot stop is utilized. The infrared source is a temperature stabilized ceramic source which operates at 1400°K. The detector is a temperature stabilized, coated fast recovery deuterated triglycine sulphate (FR-DTGS) detector with moisture resistant CsI windows. The instrument was not fitted with a more sensitive mercury cadmium tellurium (MCT) detector, but, the FR-DTGS detector was found to be more than adequate for this research. The beam size at the focus is 8 mm at the first sample position. The frequency range that may be

measured with this machine is 4400 - 400 cm^{-1} and the frequency accuracy is 0.01 cm^{-1}. A helium/neon laser is used as a reference. The ordinate precision is better than 0.1% and is usually limited by the noise level. The signal-to-noise ratio is higher than 0.1% transmittance from peak to peak. The resolution may be changed and is available from 2 to 64 cm^{-1}. The scanning times are very short, about one second is need for a scan at a resolution of 4 cm^{-1}. The sample alignment when an accessory is used is carried out with the laser and the facility exists for energy transmitted optimum alignment (Perkin-Elmer, 1984). The spectrometer is equipped with a Barnes Analytical/Spectra-Tech "Collector" diffuse reflectance accessory which will be discussed in greater detail in the next section.

The initial diffuse reflectance measurements for this research were made with a Bruker IFS 45 bench top spectrometer. However, the data handling software available with the Perkin-Elmer was more compatible with the goals of this research. Thus, the diffuse reflectance measurements were made on the Perkin-Elmer and the Bruker FT-IR was used exclusively for infrared microscopy.

The Bruker FT-IR instrument utilizes a high throughput Michelson interferometer with single air bearing controlled by a helium/neon laser. The beam splitter is KBr coated with germanium and the detector is a deuterated triglycine sulphate (DTGS) type with a KBr window. The frequency range covered by the instrument is 4800 - 400 cm^{-1} and the highest resolution available, 2 cm^{-1}, is constant over the entire range. The frequency precision is 0.01 cm^{-1} and the accuracy and repeatability is 0.1% transmittance. The aperture ratio is f/4.5 and the beam size at the sample position is 10 mm (Bruker Technical Information). The Bruker FT-IR system does not have a microprocessing unit with specialized software for data handling, although, the spectra data may be stored on floppy disks.

Diffuse reflectance accessory

There are several designs for diffuse reflectance accessories which vary in the optical alignment. The system developed by Fuller and Griffiths (1978) is shown in Figure 3.1. It is an on-axis reflectometer with ellipsoidal collection mirrors. In the original system, the collimated beam from the interferometer is reflected by two plane mirrors to a paraboloidal mirror which is at 90° to the axis of the radiation beam. This mirror focuses

the beam onto the powdered sample in a sample cup which is located at one focus of an ellipsoidal mirror. There is a small hole drilled in the ellipsoidal collection mirror at the centre on the major axis which permits the radiation from the paraboloid to pass onto the sample. With this arrangement, the specularly reflected radiation component from the sample passes back through the hole. The diffusely reflected radiation is collected by the ellipsoid and focused at the other principal focus of the ellipsoid mirror. A second paraboloid mirror positioned 90° off-axis is used to focus the radiation into a beam of about 2 mm in diameter onto the detector. A trigylcine sulphate (TGS) and a MCT detector were both used, the MCT detector requiring less scanning time. It was suggested that a state-of-the-art FT-IR equipped with a new TGS detector could be used satisfactorily, however (Fuller and Griffiths, 1978).

In later work, the ellipsoidal collecting mirror is replaced by a paraboloidal mirror with the hole drilled at the vertex. A wide beam MCT detector is also substituted for the narrow beam detector so the beam does not need to be attenuated (Fuller and Griffiths, 1980).

There are several diffuse reflectance accessories available commercially which fit into the sample compartment of FT-IR spectrometers. The accessory used for this thesis was manufactured by Barnes Analytical/Spectra-Tech Corporation and is known as the "Collector". Another commercial accessory which is often ecountered in the literature is the "Praying Mantis" which is marketed by Harrick Scientific Corporation. The designs of the various commericial accessories are illustrated in Griffiths and de Haseth (1986).

Each of the commercial accessories is designed to collect the total reflectance of the sample which is all of the specularly reflected portion and part of the diffusely reflected radiation unlike the Fuller and Griffiths design which eliminates the specular element. In several of the commercial accessories, the spectral component can be eliminated. The Spectra-Tech design incorporates a post or blocker to deflect the specular component, which will be discussed in more detail below. The Harrick design reduces the specular reflection by rotation of the plane of the sample cup (Griffiths and de Haseth, 1986).

The high efficiency of the Fuller and Griffiths design and of the commercial designs make it possible to record high quality spectra with the use of a DTGS detector as well as an MCT detector (Griffiths and de Haseth, 1986).

The optical system and the path of the radiation through the "Collector" accessory are illustrated in Figure 3.2. In this design, four flat and two aspherical reflectors are used with an alignment mirror which may be placed in the sample position (M4). The aspheric mirrors are off-axis ellipsoids which focus and collect infrared radiation with a 6x condensation of the beam. A FT-IR beam normally has a 3 to 18 mm spot size at the focus. Thus, the spot size with the diffuse reflectance accessory will range from 0.5 to 3.0 mm. The collection angle is a full pi steradians which captures 50% of the available diffuse energy. The collector accessory has been designed for high energy throughput (Barnes Analytical Technical Information).

The sample cup is removable for sample loading and can be put in place by sliding the ellipsoids apart. The sample cup is mounted on a sliding arm which brings the cup forward under the ellipsoidal mirrors so it may be removed by moving the

ellipsoids. The sample height is adjustable. The mirrors are uncoated aluminium and care must be taken not to scratch them. Four sample cups are supplied with the accessory, two macro cups which are a 13 mm in diameter and 2 mm in depth, and two micro cups which are 3 mm in diameter and 2 mm in depth. There is no vignetting of the beam with the macro cups, but some vignetting of the diffuse energy is caused by the rim of the micro cup which lowers the energy throughput. The surface of the powder in the cups should be smooth. The "Collector" may also be utilized to measure high quality specular reflectance spectra of films and coatings by positioning the sample at a 50° mean angle of incidence.

The problem of the specularly reflected component of the total energy which reaches the detector is eliminanted by the use of a blocker device on the "Collector" accessory. The device blocks the front surface of reflected energy directly at the sample. This prevents the energy from reaching the collection mirror and the detector. The effect is illustrated in Figure 3.3. A thin metal blade just touches the surface of the sample and perpendicularly bisects the sample surface without penetrating into the sample. Thus, only the infrared energy which penetrates

to some extent into the powdered sample can reach the detector. The specular component or energy reflected without penetration into the sample is prevented from reaching the collection mirror (Messerschmidt, 1985). The use of the blocker also reduces the energy throughput to only 15% of the throughput without the blocker. Thus longer measurement times and the use of a high sensitivity MCT detector are recommended. The blocker device may be moved out of position for higher energy throughput measurements when Kubelka-Munk calculations (quantitative measurements) are not necessary (Messerschmidt, 1985).

FT-IR microscope

The microscope used in the project was designed by Bruker. The accessory was designed to have high sensitivity, easy conversion between sampling modes, visible control of measured area and easy sample handling. The microscope was designed with reflecting optical elements only in the measurement channel. The instrument is fitted with interchangeable horizontal sample stages which may be controlled with computer guided stepping motors for "sample mapping" and manual switchover between reflectance and transmittance modes of measurement. The microscope has binocular optics and a movable field of view which permits convenient

inspection of the sample area. The optical system provides optimum sample illumination for reflectance and transmittance measurements. There are three types of aperture: iris, various fixed round apertures or four independent knife edges which may be utilized to isolate the desired sampling area. Sensitive detection is provided by a cryogenic detector. The detector element size may be specifically chosen for sample diameters in the range of 20 - 500 microns. The magnification and measurement area may be altered for specific purposes by exchanging objectives and apertures. The sample area space may be enlarged when the reflection mode is utilized for analysis of large or bulky samples (Simon, nd).

Experimental procedure for diffuse reflectance

General procedure

Krishnan and Ferraro (1982) have outlined a procedure for measuring diffuse reflectance spectra with a KBr powder matrix. A background spectrum of the stock powdered alkali halide powder is recorded and stored. The spectrum of the sample is then measured. The material may be diluted in stock alkali halide at a sample concentration of about 5 - 10% to obtain optimum spectra, but the spectra of undiluted samples may be measured if

necessary. The reflectance spectrum may be determined from the ratio of the sample spectrum to the reference spectrum. The procedure used for the research reported in this thesis is similar, but there are differences, mainly in sample preparation.

A preliminary report on the technique developed in this thesis has been published (Shearer, 1987). A reference spectrum of the blank silicon carbide paper is recorded in the background memory channel. The blank silicon carbide paper is then rubbed against the object or substance to be analysed until a small, but visible amount of powder adheres to the silicon carbide paper. When a sample has been removed from the object, it may be held with forceps and rubbed directly onto the paper. The sample spectrum is then measured directly from the silicon carbide paper. The Perkin-Elmer FT-IR is equipped with a microcomputer with sample handling software designed to store the reference material in a library and to compare sample spectra to the data base. If the spectrum is that of a reference material of a known identity, it is added to the reference spectra library database in the computer using the software. A spectrum of an unknown is compared to the reference library using the search software and a list of possible structural units present in the unknown compound

and a list of possible identities are produced along with a factor which gives an indication of the closeness of the fit of the unknown with each of the reference spectra. The spectrum of the unknown is then compared visually with those suggested by the search before an identification is made (Shearer, 1987).

Instrument preparation

The instrument is first aligned with the diffuse reflectance accessory and the alignment mirror in the sample position. The alignment adjusts the beamsplitter for maximum energy throughput (Barnes Analytical Technical Information) and this procedure was carried out at the beginning of each experimental session.

Background spectra collection

It is necessary to measure a background spectrum to remove the bands which result from water and carbon dioxide in the atmosphere within the instrument from the sample spectrum. If a sample medium is used, any contributions to the spectrum from the medium may be removed by including the material in the reference spectrum. The reference spectrum is collected in the background memory channel and is used for each sample measurement until it is replaced by a new background spectrum. A new reference

spectrum should be acquired if the amounts of water vapour or atmospheric carbon dioxide have changed since the last background measurement (Perkin-Elmer, 1984). This may be determined by the presence of a doublet or a valley in the region of 2360 cm^{-1} in the spectrum due to the carbon dioxide in the atmosphere.

For improved background subtraction in transmittance measurements, a sample shuttle may be used which consists of two sample holders on a stage which is controlled by a motor. The rear holder is used for the reference material with no sample and the front holder is used for the sample. The shuttle may be manipulated by the computer to move back and forth to collect a series of sample and background spectra. This allows for the sample spectra to be compared to very recently acquired background spectra and eliminates the atmospheric interferences from the final spectrum (Perkin-Elmer, 1984).

For diffuse reflectance measurements, the sample shuttle cannot be used. The background spectrum must be measured through the instrument because the pathlength through the accessory is longer than the open beam pathlength. In this work, the blank silicon carbide paper was included in the reference spectrum. The

overall reflectance of the abrasive paper is not as high as KBr and most of the sample measurements were above 100% absorption. However, the focus of this work is qualitative identification and it was considered to be more important to have consistent subtraction of background interferences than to achieve circumstances appropriate for quantitative analysis.

Slight changes in pathlength of the accessory such as a change in the position of the ellipsoidal mirrors result in inadequate subtraction of the background interferences. It is thus desirable to remove the reference material and replace it with the sample by sliding the arm out rather than by moving the ellipsoidal mirrors apart. Theoretically at least, a number of sample spectra may be measured against one background measurement. In the accessory used for this research, however, the ellipsoidal mirrors were not held together tightly and the very light disturbances which are caused by moving the sliding arm cause changes in the pathlength and the appearance of bands due to atmospheric carbon dioxide. This also sometimes occurs when the reference is removed causing interferences in the first spectrum which is measured. Owing to the time constraints within which the experimental work was conducted and the fact that the

carbon dioxide bands occur approximately in the region of 2360 cm^{-1} which is not an important diagnostic area, a reference spectrum was obtained at the beginning of each experimental session. A new reference spectrum was collected only when the carbon dioxide absorption was as intense as the weak absorption bands in the sample. Thus, the appearance of a doublet in the region of 2360 cm^{-1} in the data in this work is simply due to experimental difficulties and not in any way characteristic of the sample.

Sample spectra collection

The energy throughput should be maximized before each measurement of the reference or sample. With the "Collector" accessory, the energy throughput may be monitored in the throughput mode where the amount of energy passing to the detector is displayed. The height of the sample stage is adjusted until the reading is maximized. The sample stage height must be readjusted for each sample because the infrared radiation penetrates to different depths depending on the sample loading which affects the optical path of the attachment (Barnes Analytical Technical Information).

The instrument measures the interferogram of the sample and the spectrum is calculated by the electronic unit using the Fourier transform. The interferometer is a single beam instrument, thus the sample spectrum must be calculated from the ratio of the spectrum obtained with the sample in the beam against the background spectrum measured without the sample. The resulting spectrum is stored in one of the three memory channels and displayed on the VDU. When multiple scanning is utilized, the average spectrum is automatically calculated. (Perkin-Elmer, 1984)

The reference and sample spectra were collected under uniform instrumental conditions. One hundred scans were recorded at 8 cm^{-1} resolution in 5.2 minutes. The operational parameters were set by the engineers for optimal normal usage when the machine was installed (Perkin-Elmer, 1984). It is beyond the scope of this thesis to discuss these parameters in depth. They are, however, reviewed in the book by Griffiths and de Haseth (1986).

Sample preparation for diffuse reflectance

The silicon carbide paper used in this research was English Abrasives Waterproof silicon carbide paper, grit size p320A. In

order to maintain consistent particle size, the same grit size was used for all reference material and sample spectra. Although the interferences from the silicon carbide paper are very slight, silicon carbide paper from the same roll of paper was used for all measurements. The standard size of paper used was a 12 mm diameter circle. This size of paper was used for all standard reference spectra and for most of the unknown samples.

The majority of the unknown samples were removed by the conservator treating the object and given to the author for analysis. The sample was placed on the circle of silicon carbide paper and crushed with the back of a microspatula. If the silicon carbide was no longer visible under the powdered sample, the silicon carbide disk was held by forceps and shaken slightly to remove excess sample. A minimum of sample is required to avoid distortion of the spectra as discussed in the previous chapter. In many instances, more sample was provided than was needed. It was desirable to remove the sample with the silicon carbide paper directly from the object whenever possible. It was frequently possible to take a scraping from the reverse or an edge which was not visible while on display. The silicon carbide paper method caused minimal scratches on the objects. It was especially

suitable for varnishes or other coatings on large objects such as furniture. The method is portable, objects could be analysed without bringing them to the laboratory. Decisions on sampling method were made individually for each object in consultation with the conservator.

The basic technique was adapted to sample a series of modern sculptures in the Tate Gallery made of plastic materials. The samples are discussed in greater detail in chapter 11. It was necessary to minimize the amount of sample removed and the marks left by the silicon carbide paper as most of the plastic was transparent. The sampling marks were only visible under a microscope (Heuman, personal communication). Smaller circles of a diameter of 5 mm were punched from a finer grit of silicon carbide paper (p400). The small circles were mounted onto wooden dowels with Blue Tack adhesive and used to remove the sample. The dowels were then secured in foam and transported to the laboratory where they were measured against the background of the same blank silicon carbide paper.

Difficulties with the silicon carbide paper technique

The silicon carbide sampling technique was most successful with

solid materials which powdered easily. There were three types of samples which were more difficult to handle, samples which did not grind easily, sticky materials and specimens which contained a large proportion of inorganic matter.

Care must be taken in the interpretation of spectra of materials which are difficult to grind. Very hard materials sometimes removed some of the grit from the paper. Thus, there was a risk of interferences from the organic adhesive. Samples of birch bark bistre (hardwood pitch) were difficult to grind because of their hardness and a spectrum with very little detail was obtained. A possible solution for very hard samples is to grind the material in an agate mortar and pestle before spreading onto the silicon carbide paper.

Several samples of aged adhesive were removed as slivers of thin films and were rubbed against the paper with the back of a microspatula. The samples did not powder well. The resulting spectra were difficult to interpret and probably not representative of the intended sample as an identical spectrum was obtained by rubbing a blank silicon carbide disk with the back of a clean microspatula. In an attempt to deal with this

problem, the thin films of adhesive were held with a pair of very fine tweezers and the films were very gently rubbed onto the paper until a thin deposit formed. This technique is much more time consuming, but excellent spectra were obtained (Chapter 14).

Another problem was encountered with liquid or sticky samples. Reference materials such as Venice turpentine, gum labdanum, softwood pitch and certain waxes formed a coating on the silicon carbide paper and the resulting spectrum showed indications of specular reflectance. The problem was not remedied by the use of the blocker device as the silicon carbide paper sat in the base of the cup and the blade did not come into contact with the sample surface. A solution to the problem was found by rubbing the sticky material with powdered KBr on the silicon carbide paper. The spectrum is then recorded after a reference spectrum of the blank silicon carbide paper rubbed with powdered KBr was first measured. The effect may be seen in Figure 3.4 where a sample spectrum which was obtained with no treatment is compared to a spectrum which was measured with the sample mixed with powdered KBr. Although none of the samples taken from objects were in a liquid form, some were sticky. The samples which were extracted from the ship luting (Chapter 7) were observed to be

very sticky after the evaporation of the solvent. The samples were mixed with ground KBr and satisfactory results were obtained. Some samples taken from Egyptian jars (Chapter 5) were also very sticky.

The third class of materials which were difficult to characterize were samples which were largely inorganic in composition. Materials were classified as inorganic by the absence of bands due to C-H stretching and bending vibrations and by the presence of very broad, intense and ill-defined bands in the spectrum especially below 1200 cm^{-1} which may be due to silicate materials. Mineral matter often causes specular reflectance and a more realistic spectrum may be obtained by diluting the sample on the silicon carbide paper with powdered KBr. The focus of this research was the characterization of organic materials and no collection of inorganic reference samples was attempted for this study.

Data handling

After the spectrum was recorded, it was transferred to the microcomputer system and then saved on a floppy disk. This storage method was used as a large number of spectra were

acquired for this project. The data may then be recalled from the disk and placed in the memory of the computer for further data manipulation, printout or computer library searches. The software, CDS-3, was written by Perkin-Elmer engineers specifically for infrared spectroscopy. The expansion function was used extensively for this work to enhance detail in the spectrum especially when a small sample was used. The calculation of frequency values by the PEAK function is more precise than reading from the chart and the frequency values quoted in the thesis are those given by the computer. The spectra subtraction function was only used in a few cases when one component of a system was easily identified in the spectrum. These examples are noted in the text.

The SEARCH-3 program was developed as an aid to interpretation and identification of infrared spectra. The software contains a large data file of absorption bands which are characteristic of particular functional groups. In the interpretive section of SEARCH-3, the peak table which is generated from the sample spectrum is compared to the data base. This gives an indication of the functional groups within the molecule. The list of possible function groups or structural units (PSU) are compared

to those of the sample and the PSU's which fulfill the criteria are listed on the screen. The identification is further assisted by the comparison of the sample peak table to those contained in the SEARCH libraries. A general spectral library is included with the system and other libraries may be purchased. The software also enables the analyst to build libraries with spectra measured in the laboratory (Perkin-Elmer, 1984).

The computerized SEARCH-3 results are not conclusive and are merely intended to assist in identification of compounds. The complete list of possible structural units is compiled along with possible sources of interference in a reference manual provided with the the software and should be consulted. A definite characterization should only be made after comparison of the unknown spectrum to those in the reference volumes which were suggested by the SEARCH program or with reference spectra acquired by the analyst.

Identification of unknowns

Two methods for characterization of unknowns were used in this thesis. The first involves the SEARCH software described above and reference spectra libraries. The second technique is to

assign the absorption bands in the spectrum to specific functional groups using tables and books compiled from the characterization work in the scientific literature. The princip source for the band assignments is The Infrared Spectra of Complex Molecules, by L. J. Bellamy and the references contained therein. A combination of both methods has been used.

The commercial libraries of infrared spectra consist principally of pure chemical compounds used in chemical laboratories. They do not, however, contain materials such as the natural products which are of interest to museum scientists. A library of spectra was thus compiled incorporating the diffuse reflectance spectra of the natural product reference materials. The commercial libraries were very useful, however, for the identification of the semi-synthetic and synthetic polymer samples (Hummel, 1978; Chicago Society of Coatings Technology, 1980; Hanson, 1987).

The identification of natural products is, however, somewhat more complicated. For pure chemical compounds, an exact match between the unknown sample and the reference spectrum is required for identification. With natural products, it is more difficult because there is a great deal of similarity in infrared spectra

between a related series of compounds. The absorption bands characteristic of certain functional groups are well documented. The assignment of every band in the spectrum to a specific functional group is not always possible, however, due to spread and overlap of bands. The infrared spectrum of a complex mixture such as a natural resin contains a large number of absorption bands and they often overlap to a great degree and result in broad envelopes or bands of absorption with few distinctive peaks (Mills and White, 1987).

An example is given in Mills and White (1987) which compares the spectrum of a pure compound, hydroxydammarenone I, which is present in fresh dammar resin, unaged dammar resin and a dammar varnish film which is 50 years old. There are many strong, sharp bands in the region of 1300 - 625 cm^{-1}. The same region is somewhat blurred in the spectrum of the fresh dammar resin, although there are bands present which may be assigned to individual substituents. The aged sample is increased in chemical complexity and this results in several broad, indistinct bands in the spectrum (Mills and White, 1987).

Experimental procedure for thin layer chromatography samples

Preparation of thin layer chromatography samples

An attempt was made to measure the diffuse reflectance spectrum of spots from high performance TLC separations. A CAMAG HP-TLC Arid Chamber system was used with precoated silica gel plates (60F254). Two different solvent phases were used, a 50:50 (v/v) solution of heptane and t-butylmethylether and a 50:50 (v/v) solution of methanol and t-butylmethylether. Various materials which are typical of the natural products being analysed from archaeological collections were analysed using both solvent systems. These include glance pitch, frankincense, stick lac, abietic acid and Pistacia lentiscus. The resulting plates were allowed to dry and the plates were examined under fluorescent and ultraviolet light without any chemical development. The spots were scored around with a scalpel blade under the fluorescent light and removed by sliding the scalpel blade under the spot and lifting it from the glass support. A blank was obtained in the same manner and a reference spectrum was measured of the silica gel. A spectrum of the sample spot was then recorded, but the spectrum was distorted, perhaps by specular reflectance from the surface of the sample. The sample spots were then analysed using

silicon carbide paper. The reference was obtained by rubbing the silicon carbide paper with silica gel which had been treated with the solvent system, but not the sample. The sample spots were removed and measured in the same way. The resulting spectra were very similar to one another and characterized by a broad band centered at about 3400 cm^{-1} and broad, indistinct bands from 1650 - 400 cm^{-1} with a very strong, wide band in the region of 1200 - 1000 cm^{-1}. In some cases, a very weak sample spectrum was observed but after abscissa expansion, the compensation for the broad band at 3400 cm^{-1} was too strong in relation to the other bands resulting in a negative absorption. The general similarity of the spectra to each other and the complete absence of bands due to C-H stretching indicated that there were spectral interferences from the silica gel. The commercial plates contain inorganic fluorescing agents and binders which may cause interferences. Also, rubbing the spot onto the silicon carbide paper is an inefficient way of handling small samples and most natural products such as those used for this study do not absorb more strongly than the silica gel compound matrix.

Extraction of the sample spots from the silica gel was attempted using AnalaR diethyl ether. One trial TLC plate was made of

glance pitch, hydrocarbon wax, and abietic acid and a second plate was prepared of hexatriacontan, umbelliferone and Pistacia lentiscus. Selected spots were removed with a scalpel in the same manner and placed in a small amount of ether in capped vials overnight. The solutions were then put through a pipette which contained a plug of silica glass wool to remove the silica gel. The solutions were then placed in a fume cupboard and the ether was allowed to evaporate.

Interpretation of thin layer chromatography sample spectra

The resulting spectra were obtained by rubbing the solute left after evaporation onto the silicon carbide paper. The reference for this experiment was the blank silicon carbide paper. The spectra were similar to each other and to those obtained directly from the sample spots. However, there may be evidence of the sample in the spectra in the form of bands in the C-H stretching region (2960 - 2920 cm^{-1}) which are present in all of the spectra but not in the spectra of the blanks. The spectra do not bear a close similarity to the standard spectra of the reference materials. The spectrum of the residue extracted from the abietic acid is marked by the absence of the strong band expected in the carbonyl region (1700 cm^{-1}). The standard spectrum of

umbelliferone shows a series of many sharp, strong bands from 1510 - 400 cm^{-1} which are absent in both of the sample spectra of the umbelliferone spots which were extracted from both solvent systems. The spectrum of the umbelliferone extract from the heptane/t-butylmethylether solvent system had a very intense, broad band with its most intense region centred at 1064 cm^{-1}. (This band is probably due to the silica gel.) Likewise, the standard spectrum of the hydrocarbon wax is very simple and marked by strong bands in which are discussed in chapter 4. Only the bands due to the C-H stretching vibrations are present in the spectra of both of the extracted samples of the hydrocarbon wax where broad, intense bands are observed in the region from 1300 to 400 cm^{-1} due to interferences from inorganic materials.

The spectrum of the extracted sample spot of the glance pitch contains bands in the C-H stretching region (centered at 2917 cm^{-1}) and bands at 1607, 1475, 1361 and 1209 cm^{-1} which correspond to bands in the standard diffuse reflectance spectrum of glance pitch at 2926, 1603, 1461, 1377 and 1203 cm^{-1}. There is, however, very little similarity between the spectra in the area from 1150 - 400 cm^{-1}. There is a strong band centred at 3358 cm^{-1} and one at 787 cm^{-1} in the extract spectrum which are

interferences which are most probably caused by silica gel. The most promising results were found with the hexatriacontane, a long chain hydrocarbon with a very simple diffuse reflectance spectrum. There are strong bands in the reference spectrum at 2956, 2931, 2894, and 2857 cm^{-1} (C-H stretching vibrations), 1471 and 731 cm^{-1}. The spectrum of the extract of the hexatriacontan spot from the methanol/t-butylmethylether solvent system has bands at 2920 (multiplet), 1461 and 726 cm^{-1}. There are, however, several bands in the region of 1731 - 1580 cm^{-1} and intense bands in the region from 1200 to 1000 cm^{-1} which are not evident in the standard spectrum and are probably due to elements in the silica gel. The characteristic bands are not present in the spectrum of the extracted spot from the heptane/t-butylmethylether system where they seem to be masked by several broad, intense bands at 1434, 1352, 1196, 1004, 814 and 523 cm^{-1}.

There are several possible sources for the interferences. The contamination bands might be due to residual solvent. However, the plates were dried briefly with hot air after the chromatographic run and heated in an oven at 38°C for 30 minutes before the samples were removed. The most probable causes are the silica gel and the inorganic fluorescing agents, particularly

as the spectral features are similar to those observed with inorganic materials, i.e. broad, ill-defined, very intense bands. It is possible that the background subtraction is not entirely adequate in compensating for the silica gel. This difficulty was encountered by other workers (Fuller and Griffiths, 1980). The extraction process could also be improved by filtering the solution through a sintered glass filter to remove finely suspended silica gel from the solvent as suggested by Fuller and Griffiths (1980). The extraction might also be more efficient if a solvent in which the solute is more highly soluble were chosen. The choice of such a solvent is, however, difficult with unknown samples. The treatment of the silica gel plate with a releasing agent might also improve the recovery of the specimen.

The difficulty in obtaining satisfactory spectra of standard materials of known identity and the problems encountered by other workers (Fuller and Griffiths, 1980) suggested that this method is not suitable for analysis of archaeological specimens. It would be more desirable to perform a sensitive separation technique such as HPLC or GC-MS if a multicomponent system is suspected.

Experimental procedure for FT-IR microscopy

The procedure for obtaining spectra with the microscope is similar to that for measuring diffuse reflectance spectra. Infrared microscopy is single beam transmission spectroscopy and it is necessary to record a reference spectrum. The supporting material for the sample is included in the background spectrum which is stored in the background channel. The sample interferogram is then recorded and the computer calculates the spectrum, subtracts the background and displays the spectrum. The spectrum is then stored on magnetic disks for future reference, although no software facilities existed on the machine for the collection and storage of a search library. The spectrum may be manipulated on the screen and enlarged printouts may be made.

The major difficulty with the microscope is the sample preparation. There are two problems with sample preparation for infrared microscopy. The first difficulty is in mounting the sample and the second is in obtaining satisfactory sample thickness and transparency. Most conventional mounting techniques for microscopic specimens require synthetic resins or glass slides, both of which would cause too much contamination to

achieve a worthwhile spectrum. High pressure diamond anvil cells are one possible solution, but one was not available for this research. The original analyses in this thesis were carried out using blank KBr disks (13 mm in diameter). The sample was placed on the disk and then a small amount of solvent was deposited onto the disk. It was hoped that the solvent would dissolve all or part of the sample and the transmission spectrum could easily be measured. The difficulties encountered with this technique were loss of sample and insoluble samples. The method which was adopted involved the use of copper transmission electron microscopy (TEM) grids. The sample was transfered to the grid with microforceps and pressed with manual pressure with the back of a clean microspatula. The small particles of sample adhered to the grid which left portions of sample supported, but with no backing which would cause spectral interference in the infrared. The grid was supported in an aluminium disk which had a 2 mm hole drilled through it and a 4 mm shallow depression to hold the grid in place. The aluminium disk was placed on the microscope stage which could be moved by two micrometers to align the sample. This method allowed for the examination of materials with very little sample manipulation. Although the sample thickness was

not measured directly, the amount of energy throughput was used to determine if the sample was thin enough. The reference spectrum was collected by moving the circular aperture to 1.05 microns and position the aperture in one of the empty square openings in the grid. The reference spectrum of 200 scans was obtained at 8 cm^{-1} resolution and had an energy throughput of approximately 2000 counts per unit time. The sample spectrum was obtained by moving the sample using the movable stage so that a fairly transparent section of the sample within an open square of the grid was visible in the aperture. The energy throughput of the various references and unknowns were different. Very thin, transparent samples could range from 1000 - 1500 counts per unit time. Some spectra were obtained with counts as low as 262, but the sample was then usually pressed a second time or a different location on the sample was chosen to obtain an energy throughput of 400 counts per unit time or more. In some cases, the sample did not fill the grid entirely and a small amount of light passed through. This resulted in the presence of bands in the region of 2360 cm^{-1} which are due to inadequate compensation for the carbon dioxide from the atmosphere.

Figure 3.1 Diagram of diffuse reflectance FT-IR system developed by Fuller and Griffiths (1978). (S) is the sample, (P) are the paraboloidal mirrors, (E) is ellipsoidal mirror and (D) is the detector.

Figure 3.2 Optical diagram of the "Collector" diffuse reflectance unit (Spectra-Tech Corporation) (Griffiths and de Haseth, 1986).

Figure 3.3 Diagram of blocker device for use with the "Collector" accessory (Messerschmidt, 1985). (A) represents the specularly reflected radiation reflected back to the source by the blocker and (B) represents the diffusely reflected radiation directed to the detector.

Figure 3.4 Diffuse reflectance FT-IR spectra of (a) softwood pitch (RW1 Pix liquida) (gsva0015) and (b) softwood pitch mixed with KBr powder (RW1) (gsva0615).

CHAPTER 4 WAXES

Beeswax

Source

Wax is produced by species of the Apis bees (Mills and White, 1987). It is manufactured by the bees using wax glands in their abdominal wall. The thin scales of wax are used to construct the comb and then it is filled with honey. To recover the wax, the honey is removed by draining and centrifuging. The wax is then heated in water and filtered. The natural product is a pale yellow colour and may be bleached by the sun or by oxidizing agents (Tooley, 1971).

Composition

The chemical composition of beeswax seems to be consistent. Eighty samples of Canadian beeswax were examined (Tulloch and Hoffman, 1972) to determine the quantitative values of acid, ester and hydrocarbon composition. The values were observed to fit into narrow ranges. There was little variation between values obtained from old comb waxes and pure capping wax. The percentage of hydrocarbons was found to be slightly higher for older waxes. There were no significant differences between waxes collected from different regions of Canada (Tulloch and Hoffman,

1972). Beeswax is produced by bees and not collected from plants and the composition is determined biogenetically and is thus consistent (Mills and White, 1987). The differences in composition between different species of bee have not been examined, however. It is known that beeswax from the African species Apis mellifera adansonii is very similar in composition to that of the common Apis mellifera. In contrast, ghedda wax which is obtained from Asiatic bees was found to be similar in qualitative composition, but very different in quantitative composition (Mills and White, 1987). The principal components of beeswax are mono-, di-, poly- and hydroxy esters, free acids, and hydrocarbons (Tulloch, 1972). The composition of beeswax is given in Table 4.1 (Tulloch, 1971).

Beeswax is one of the first ancient materials to have been identified with a reasonable degree of certainty. Early samples were identified using the melting point. The melting point range for the eighty Canadian wax samples was 63.5 - 65 °C (Tulloch and Hoffman, 1972) and it is fairly consistent for aged samples as well (Mills and White, 1987). Infrared spectroscopy (Kuhn, 1960) and later gas chromatography (White, 1978) were recommended for identification of waxes. Infrared spectroscopy is suggested for

relatively pure samples if sufficient sample is available as the spectrum is not affected much by oxidation. Exposure to water during burial may cause partial hydrolysis (Mills and White, 1987).

Identification and interpretation of standard spectra

Kuhn (1960) has published spectra of various waxes including pure and adulterated beeswax. The standard spectra measured in this study are very similar to those given by Kuhn. For this thesis, two commercial beeswaxes and six obtained from the British Museum (Natural History) of various Apis species were analysed and the ranges of major bands are given in Table 4.2. A sample of wax produced by a Trigona species was also measured and the frequency values are listed separately in Table 4.2. The samples obtained from the British Museum (Natural History) were taken from the combs. In one case, the comb had been abandoned and bleached white by the sun. In the other examples, the comb was coated with material thought to be a combination of residual polysaccharide and dust. The spectrum of the naturally bleached sample is given in Figure 4.1a and was found to be most similar to those of the commercial beeswaxes and those published by Kuhn. The spectra of the other samples from the combs are also very

similar, but they exhibit a more pronounced absorption in the hydroxyl region and several of the spectra exhibit two absorptions in the region of 1650 and 1550 cm^{-1}. These interferences may be due to residual polysaccharide material or, more probably due to hydrolysis of the sample. These spectra also exhibit a lower relative intensity of the bands in the region 1400 - 400 cm^{-1} which may result from inorganic interferences from dust.

The major difference between the spectra measured in this study and that of Kuhn is that the resolution in the C-H stretch region is much better in the more recent spectra. In Kuhn's spectra, there is one absorption band with maximum intensity in the region of 2850 cm^{-1}. In the reference spectra in this study, the separate bands are more distinct and occur in the ranges of 2932 - 2935 cm^{-1}, 2894 - 2904 cm^{-1} and 2856 - 2859 cm^{-1}. The bands in the ranges 2932 and 2856 cm^{-1} result from the C-H stretches in the methylene groups and the band in the region of 2894 cm^{-1} is due to a combination of methyl groups and methine C-H stretches (Bellamy, 1975).

The band which appears in the carbonyl region at 1736 - 1741 cm^{-1} in this study occurs at 1730 cm^{-1} in the spectrum published by Kuhn and assigned to the C=O stretch in the ester functional group. The range given by Bellamy (1975) is 1750 - 1730 cm^{-1} for normal saturated esters. Kuhn also mentions a second, weak band at 1709 cm^{-1} which appears as a shoulder on the band at 1730 cm^{-1}. Mills and White (1987) have published a spectrum with two distinct bands located at 1738 and 1711 cm^{-1} with the latter band having a weaker intensity. The second carbonyl band results from the C=O stretch in the un-ionized free carboxylic acids present (Kuhn, 1960; Mills and White, 1987). The carbonyl region in the spectra obtained in this study resemble those in Kuhn with a weak shoulder present on the carbonyl band near 1710 cm^{-1}. The range for C=O vibrations in saturated aliphatic acids is 1725 - 1700 cm^{-1} (Bellamy, 1975).

The beeswax standard spectra exhibit bands in the ranges 1474 - 1470 cm^{-1} and 1379 - 1377 cm^{-1} which are due to C-H deformations or bending vibrations. The absorption band in the region 1474 - 1470 cm^{-1} is due to a combination of the -CH2- groups and the asymmetrical deformations in the -CH3 groups and the band in the region of 1379 - 1377 cm^{-1} results from the symmetrical -CH3

bending vibration (Bellamy, 1975). The values quoted in the literature for beeswax are 1470 and 1388 cm^{-1} (Kuhn, 1960). The spectra obtained in this study also contain weak absorptions in the region 1420 - 1418 cm^{-1} and near 1347 cm^{-1}. They appear in the spectrum in the literature, but are not assigned. They fall beyond the usual limits for C-H deformation frequencies which rarely deviate more than $\pm$ 20 cm^{-1} from the values 1450 and 1465 cm^{-1} or from 1380 - 1370 cm^{-1} except in the presence of a strongly electronegative atom (Bellamy, 1975).

An intense absorption occurs in the region of 1179 - 1176 cm^{-1} in the spectra obtained in this study which corresponds to the band at 1177 cm^{-1} in the literature and is assigned to the C-O stretch in the ester functional group (Kuhn, 1960). This band occurs in addition to that in the region of 1730 cm^{-1} which are characteristic of the ester group. The range for the C-O stretching vibration is 1200 - 1150 cm^{-1} for propionates and higher esters (Bellamy, 1975).

The spectrum given in the literature (Kuhn, 1960) exhibits weak absorptions at 962, 918, 890 cm^{-1} and a series of six absorptions between 1333 - 1190 cm^{-1} which are unattributed, but are thought

to be characteristic of solid beeswax as they disappear when the substance is examined in the molten state. Nine bands are present in the spectra obtained in this study in the regions 959 - 958 cm^{-1}, 922 - 921 cm^{-1}, 891 - 866 cm^{-1}, 1331 - 1330 cm^{-1}, 1312 -1311 cm^{-1}, near 1267 cm^{-1}, 1246 - 1245, near 1221 and 1198 - 1197 cm^{-1}. The bands in the region 1350 - 1180 cm^{-1} may be assigned to a phenomenon known as a band progression present in fatty acids and fatty acid esters which result in a series of evenly spaced bands in this region. They are thought to be due to rocking and twisting motions of the methylene groups (-CH2-) in the trans- configuration in the aliphatic chains, (Jones et al., 1952). Conditions which modify the structure affect the spectrum. The disappearance of the absorptions in spectra of material in the liquid state is thought to result from a continuous and random distribution of the aliphatic chains (Bellamy, 1975, Corish and Davison, 1955). One trial spectrum of commercial beeswax which was not included in the values given in the table was obtained when the sample was still very sticky. As a result, the spectrum showed evidence of specular reflection in the higher frequency region. However, all of the major absorptions were present at slightly varying frequency values and

the bands which are characteristic of solid beeswax in the region of 1330 - 1190 cm^{-1} were absent in the spectrum of the sticky wax.

Kuhn's report mentions the presence of a doublet at 730 and 719 cm^{-1} in the beeswax spectrum which was attributed to the presence of long chain hydrocarbons. These absorptions appear as a single band in the reference spectra in this study in the region 729 - 722 cm^{-1}. The range given by Bellamy (1975) is 750 - 720 cm^{-1} for a chain of four methylene groups or more.

In the report published by Kuhn, spectra were presented of beeswax mixtures. The first example was that of Punic wax. The process of preparing Punic wax has been reported by ancient sources. By this method, beeswax is heated with seawater and soda (Pliny, Book XXI, line 84). The soda reacts with some of the esters producing sodium salts of the fatty acids (soaps). The resulting mixture can be emulsified with water and used as a paint medium. Punic wax was produced by Kuhn with beeswax, water, and sodium carbonate, and a spectrum was obtained of the dried film. The spectrum is similar to that of beeswax with several minor discrepancies. The band at 1480 cm^{-1} is widened on

the low wavenumber side, and a new band appears near 1570 cm^{-1}. The changes are the result of the presence of ionized carboxyl groups of the salts of the fatty acids (Kuhn, 1960). These groups are characterized by absorption bands in the region between 1610 and 1550 cm^{-1} and near 1430 cm^{-1} (Colthup, 1950). The greater width of the band at 1480 cm^{-1} in the Punic wax spectrum as compared to the corresponding absorption in the beeswax spectrum is thought to be due to the influence of the band from the ionized carboxyl group. The spectrum of the alcohol extract of the punic wax shows weak indications of the characteristic beeswax spectrum. The bands due to the ionized carboxylic acid are stronger (Kuhn, 1960).

Two spectra were also obtained of wax-resin canvas relining mixtures (Kuhn, 1960). The mixtures were studied as films without any solvent extraction. The band at 2859 cm^{-1} in the spectra of the colophony and beeswax mixture was observed to be widened on the high wavenumber side due to additional O-H groups present. Extra carboxyl groups widen the carbonyl band on the higher wavenumber side. An increase in carboxyl groups also generates a fairly strong series of bands between 1274 - 1250 cm^{-1} which are superimposed on those resulting from the solid

beeswax. An absorption due to the $R_2C=CHR$ configuration of the resin acids also appears in the region 833 - 820 cm^{-1}. The spectrum of a beeswax and A.W.2 resin mixture (A.W.2 is a ketone resin produced as a condensation product of cyclohexanone and methyl cyclohexanone) was observed to have a strong band at 3450 cm^{-1} due to the increase in O-H groups present. Kuhn (1960) assigned the band at 1053 cm^{-1} to O-H absorptions. A weak band appears in this region in the standard spectrum and in all of the beeswax spectra obtained in this study and is probably the result of hydrolysis. The band at 1730 cm^{-1} is widened on the low wavenumber side due to the increase in ketone groups in the mixture (Kuhn, 1960).

Kuhn concludes that the infrared spectra of beeswax mixtures only indicate whether the beeswax is adulterated in some way and that separation by solvent extraction is required to identify other additives (Kuhn, 1960).

It has been noted (Mills and Plesters, 1963) that in the spectra of wax-resin mixtures, the carboxylic acids present in the resin cause a widening of the base of the C-H band in the region of 2900 cm^{-1} and that the hydroxyl absorption appears as a shoulder

on the higher wavenumber side of the bands near 2900 cm^{-1}. This was evident in sample spectra published by these authors and in the spectrum of wax-colophony mixture published by Kuhn (1960).

Identification of unknown samples

Unadulterated beeswax

A sample of a waxlike coating was removed from a Gaudier-Brezska sculpture constructed in red sandstone, Redstone Dancer (c. 1913). No record of previous conservation treatment exists and the coating may not be original. The sample was rubbed onto the silicon carbide paper for analysis. The resulting spectrum was found to correspond very closely with that of beeswax (Shearer, 1987). Characteristic bands occur in the region of 2900, 1739, 1471, 1377, 1177 and 724 cm^{-1}. The series of six bands occurs near 1330, 1312, 1290, 1266, 1220 and 1198 cm^{-1} and bands are observed at 957 and 922 cm^{-1}. A weak band occurs in the region of 890 cm^{-1} (Table 4.2). The only evidence of adulteration is a broad O-H shoulder on the C-H stretching bands which is centered at 3400 cm^{-1} which may result from hydrolysis.

A sample was removed from a large Chinese inlaid bronze vase (Victoria and Albert Museum M1154-1296) with multiple repairs.

The material of interest was a green waxy filler that fluoresced yellow and a sample was taken along a vertical edge of the neck with silicon carbide paper. The sampling marks were easily removed by gently smoothing the surface with a soft cloth. The spectrum obtained from the silicon carbide paper was very similar to that of the beeswax spectra. (Table 4.2). The only evidence of impurities present is the rounded absorption centered at 3331 cm^{-1} and several weak absorptions around 779 cm^{-1}. However, the remaining regions of the spectrum are very sharp and there is very little other evidence of adulteration.

A sample was taken with silicon carbide paper of an Egyptian figurine which was thought to be made of wax (Boston Museum of Fine Arts 72.4783). The sample was obtained on silicon carbide paper in Boston and transported to England to be analysed. The resulting spectrum is extremely similar to that of pure beeswax. (Table 4.2). There is only a small shoulder on the C-H stretching bands in the region of 3350 cm^{-1} and a slight shoulder on the carbonyl absorption at 1715 cm^{-1}. There is no strong evidence of adulteration in the spectrum.

A sample was collected from a large block of wax at the probable site of a metal casters workshop from the Maligawa excavations at Kandy, Sri Lanka. (The site dates from around the 16th century.) The sample had a sandy crust on the outside and the interior more closely resembled fresh wax. A spectrum was recorded of both the exterior crust and the interior. The spectra were found to be very similar (Figure 4.2) in spite of the differences in appearance of the samples. Both of the plots contain a rounded absorption in the region of 3300 - 3360 cm^{-1} which is more intense in relation to the other absorptions in the spectrum of the weathered crust (Figure 4.2b). The band in the region of 1050 cm^{-1} is also stronger in the spectrum of the crust. These changes are probably due to hydrolysis of the material. Also, they may be the result of natural impurities such as residual carbohydrates which are visible in some of the reference spectra collected from the combs. The spectrum of the exterior material also contains weak bands at 1646 cm^{-1} (with a shoulder which ends at 1520 cm^{-1}) and at 1102 cm^{-1} which are not seen in the spectrum of the material taken from the interior of the block. These absorptions are more likely to be caused by the presence of minor impurities than by ageing.

Beeswax mixtures

An ethnographic knife handle from central Australia was examined. It was thought that the wax used to produce the handle was obtained from Trigona bees whose wax has been reported (Dickson, 1981) to have superior working properties to that of Apis species for the manufacture of experimental tools. It was also found (Dickson, 1981) that the wax prepared by Aboriginals was loaded with vegetable matter and ochre to an extent of 70% by weight. It is necessary to adulterate the wax to prevent shrinkage and add mechanical strength (Dickson, 1981). The spectrum obtained of the handle material in this study contains absorptions which are characteristic of beeswax with some unusual bands. The spectrum exhibits the series of six absorptions in the region 1330 - 1190 cm^{-1} which have been observed in the spectra of the wax of the Apis species, but not in the spectrum of the wax of the Trigona species. It would seem that the handle was produced from wax from an Apis species. However, not enough samples were available of Trigona species wax to make a firm judgement on this sample. The spectrum also contains bands at 1631, 1577, 1544 and 877 cm^{-1} which may be caused by additives and a broad band

centred at 3331 cm^{-1} which may caused by residual polysaccharide material and pollen, but more likely to be caused by hydrolysis.

A sample from a Minbar at Shiraz, Iran was examined. The sample was contaminated having been wrapped in adhesive tape for transport. The sample was removed from the adhesive tape and an attempt was made to find a fresh surface. A scraping of the adhesive tape was taken with the silicon carbide paper and included in the background spectrum in order to subtract any contribution to the spectrum from the adhesive tape. The resulting sample spectrum exhibits similarities to the beeswax spectra, but there is an overall loss of relative intensity which may be due to interferences from the adhesive tape or to the presence of other additives. However, there are bands in the region of 2900 cm^{-1} and one at 1736 cm^{-1} with a slight shoulder. Absorptions are present at 1466, 1377, 1174 and 723 cm^{-1}. There are five weak absorptions visible in the region between 1330 - 1190 cm^{-1}.

A sample was obtained of the black resinous material (MFA1) found outside the mummy Nesmin (Rhode Island School of Design). The spectrum of the sample indicated beeswax with additives (Figure

4.3a). The bands in the region of 2900 cm^{-1}, at 1736 and 1713 cm^{-1}, at 1464, 1379, 1173 and 722 cm^{-1} are indicative of beeswax and there are six very weak bands in the region 1330 - 1190 cm^{-1}. However, the band centred at 3300 cm^{-1} merges with the C-H stretching absorption which is widened at the base. The absorptions in the carbonyl region are also widened and the band at 1713 cm^{-1} is of equal intensity and indicative of the presence of carboxylic acids (Mills and Plesters, 1963). The additional carboxylic acids are evidence of a resin mixture. Also, the bands at 1464 and 1379 cm^{-1} are not as distinct as in the pure beeswax spectra and there is a shoulder to the right of the band at 1464 cm^{-1}. The mixture was analysed by gas chromatography/mass spectroscopy and found to be composed principally of beeswax with additions of resin and bitumen (White, personal communication).

Spectral subtraction with the interactive difference function was utilized with the diffuse reflectance spectrum of the sample MFA1 (Figure 4.3a) and a spectrum of beeswax from Apis mellifera (NHM19) (Figure 4.3b). The resulting spectrum (Figure 4.4) contains features which are indicative of a resin. Characteristic resin spectra are discussed in chapter 7.

A sample of wax from the surface of a burnt fragment of a Nimrud ivory was analysed (See Chapter 14). The spectrum contains evidence of beeswax and other additives. Bands are present in the region of 2900, 1739, 1477, 1379, 1176, 958, 920 and 729 cm^{-1}. There are also bands evident at 1312, 1290, 1266, 1244, 1220 and 1197 cm^{-1}. However, the region near 1500 - 1350 cm^{-1} is indistinct and not similar to the region in beeswax. The weak absorptions near 1420 and 1340 cm^{-1} are not present. There is a shoulder on the low wavenumber side of the band at 1477 cm^{-1} and two absorptions at 1539 and 1504 cm^{-1} which have been assigned by Kuhn to ionized carboxyl groups. There is also a shoulder on the C-H stretching absorption band which is centred near 3350 cm^{-1}. In addition, the spectrum also contains weak bands at 2551, 2524, 1786, 874 and 857 cm^{-1} (Chapter 6)

Spermaceti wax

Source

Spermaceti wax is obtained from the oil present in the head cavity of the sperm whale, Physeter macrocephalus L. and the oil contains 11% of the hard wax material. It has been available since the advent of whaling and was utilized in 15th century England (Mills and White, 1987).

Composition

The literature indicates that it is composed of cetyl palmitate (cetyl alcohol is the C16 alcohol as palmitic acid is the C16 acid), but further investigation with gas chromatography indicates that it contains a series of long chain fatty acid esters including ceric acid (White, 1978). The material was saponified and methylated and the resulting gas chromatography analysis gave C12 as the major acid and others were found to be present including C10 to C18 with lesser amounts of higher acids. The principal alcohols present were found to be C18, C14 and C16 and smaller amounts of C13, C15 and C17 were detected (Mills and White, 1987).

Identification of standard spectrum

A sample of spermaceti wax (British Museum Research Laboratory) was obtained and the spectrum is shown in Figure 4.5. The spectrum is characterized by bands at 2960, 2935, 2860 and 2838 cm^{-1} which correspond to the values given by Bellamy (1975) for C-H stretching vibrations (See Table 4.3). Bands are also observed at 1474 and 1378 cm^{-1} which result from the C-H deformation frequencies and correspond to the values listed in the literature (Bellamy, 1975). There are also weak bands at

1418 and 1348 cm^{-1} which occur in the beeswax spectra. There is a band in the spermaceti spectrum at 730 cm^{-1} which is characteristic of the rocking vibration of long aliphatic chains.

The spermaceti spectrum is also characterized by a strong absorption at 1741 cm^{-1} which corresponds to the C=O linkage in the ester functional group. A band is observed at 1184 cm^{-1} which is due to the C-O stretch in the ester linkage. The values correspond with the value ranges in the literature of 1750 - 1730 cm^{-1} for the C=O stretch and 1200 - 1150 cm^{-1} resulting from the C-O.

There is a pattern evident in the spectrum which is similar, but not identical, to that of solid beeswax. There are a series of weak, sharp bands at 1330, 1309, 1284, 1223 and 1202 cm^{-1} and at 984, 958, 922, 890, 851, 816 and 776 cm^{-1}. The values are not exactly the same as for the beeswax and the region between 984 - 776 cm^{-1} is more complex in the spermaceti spectrum than in that of the beeswax. The band progression in the region 1350 - 1180 cm^{-1} in solid fatty acids is thought to be related to the rocking or twisting motions of the methylene groups in the chains (Jones

et al., 1952). Thus, it is possible to differentiate between the two materials using spectra of pure samples.

The spermaceti wax spectrum is also characterized by a slight shoulder in the hydroxyl region on the the C-H stretching vibrations near 3450 cm^{-1} and a shoulder on the high wavenumber side of the carbonyl absorption which is indicative of a small quantity of carboxylic acid. The band at 1418 cm^{-1} falls within the range of the C-O- stretching of carboxylic acids, however, the band which should characteristically accompany it (a fairly intense band in the region of 1320 - 1211 cm^{-1}) is absent in the spermaceti wax spectrum. One of the bands in the region of 950 - 900 cm^{-1} may be the result of O-H out of plane deformation in carboxylic acids (Bellamy, 1975).

Carnauba wax

Source

Carnauba wax is obtained from the leaves of the palm Copernicia cerifera Mart. which is grown mainly in Brazil. The waxy coating is collected by shredding and beating the leaves which causes the wax to come off as a powder (Mills and White, 1987). This material is collected, melted with a small amount of water and poured into moulds. The resulting commercial product is the grey

impure wax. The pure wax is almost colourless with a melting point range of 82 - 90 °C (Tooley, 1971). It is used in conservation mixed with beeswax to produce a harder product with a higher melting point for relining canvases and other uses. Carnauba wax is a major constituent of wax polishes and is often mixed with less expensive waxes such as paraffin (Mills and White, 1987).

Composition

The composition of carnauba is esters of long chain alcohols and acids with longer carbon chains than in beeswax. Thus, the materials are easily separated by gas chromatography. The substance also contains triterpenes and about 50% of the material is too involatile for analysis with gas chromatography (Mills and White, 1987). The composition determined by gas chromatography as given in the literature is listed in Table 4.4 (Tulloch, 1973). The volatile portion was reported as 47% with 11% free alcohols and 36% monoesters. After methylation, the composition was found to be 27% acids, 57% alcohols, 13% omega-hydroxy esters and 3% alpha,omega-diols (Tulloch, 1973). It has also been suggested that the involatile fraction contains hydroxyesters, p-hydroxy and p-methoxycinnamic acid diesters (Vandenburg and Wilder, 1970)

although these were not detected by the gas chromatography (Tulloch, 1973).

Interpretation of standard spectra

Spectra were obtained of grey and yellow carnauba wax obtained from commercial sources and yellow carnauba wax (Copernicia prunifera) from the Museum of Economic Botany, Kew. The spectra were extremely similar and the range of observed frequency values and assignments are listed in Table 4.5. A carnauba wax spectrum is given in Figure 4.6a (Kew sample Copernicia prunifera).

There is a rounded band with maximum intensity in the region of 3337 - 3354 cm^{-1} which is due to the O-H groups in the alcohol present in the structure. There are bands in the region of 2925 - 2927 cm^{-1} and 2852 - 2853 cm^{-1} which correspond to the values given by Bellamy (1975) for C-H stretching vibrations. The spectrum also contains bands at 1470 and 1376 cm^{-1} which fall within the ranges for C-H bending vibrations listed in Bellamy. There is a relatively strong absorption at 724 cm^{-1} in the spectra that is due to the rocking vibration of the long aliphatic chains (Bellamy, 1975).

The spectra are characterized by strong absorptions in the ranges 1736 - 1737 cm^{-1} and 1173 - 1174 cm^{-1} which fall into the values quoted by Bellamy (1975) for aliphatic esters.

The carnauba wax spectra contain absorptions which indicate the presence of an aromatic ring. In the spectrum reported by Kuhn (1960), the bands fall at 1612, 1515 and 833 cm^{-1}. In the standard spectra reported in this thesis, the bands fall at 1633, 1606 - 1607, 1516 and 832 - 833 cm^{-1}. The band at 1633 cm^{-1} is a shoulder on the band at 1606 cm^{-1} corresponding to the band recorded at 1612 cm^{-1} in the literature. The vibrations are due to skeletal ring breathing modes. The values listed by Bellamy (1975) are 1625 - 1575 cm^{-1} (1650 - 1585 cm^{-1} for para-substituted materials), 1600 - 1560 cm^{-1}, 1525 - 1475 cm^{-1} and in the area of 1450 cm^{-1}. The band at 1450 cm^{-1} is often masked in spectra of materials with methylene groups which also absorb in the region. The presence of aromatic compounds is also supported by absorptions in the region of 3030 - 3079 cm^{-1} which are due to aromatic C-H stretching absorptions in these spectra. They are often masked by the strong aliphatic C-H vibrations. A shoulder can be seen at the left side of the C-H stretching absorptions which may result from the aromatic compounds.

Identification of unknown sample

A sample of the material used for reconstruction of a copper alloy vessel rim (Bedford Museum 1712) was analysed (Figure 4.6b). The sample was removed from the object for analysis and rubbed against the silicon carbide paper. The sample contained a green colouring matter which lowered the baseline in the fingerprint region of the spectrum. However, it was possible to see evidence of a wax material. The presence of bands in the region of 2922, 2852, 1734, 1469, 1419, 1379, 1174 and 722 cm^{-1} comfirmed the presence of a wax. The spectrum was not marked by the series of bands between 1330 and 1190 cm^{-1}, only two are visible at 1312 and 1243 cm^{-1}. Also, the spectrum exhibits bands at 1608 and 1588 cm^{-1} which are indicative of aromatic compounds. The absence of the sharp bands in the region 1330 - 1190 may be the result of adulteration of the material with resin, but the bands due to the aromatic compounds are suggestive of carnauba wax. The presence of a broad band at 3341 cm^{-1} which appears as a shoulder on bands centred at 2922 cm^{-1} and the second carbonyl absorption at 1713 cm^{-1} which is of equal intensity to the band at 1734 cm^{-1} are characteristic of carboxylic acids which may result from a resin mixture.

Candelilla wax

Source

Candelilla wax is obtained from various species of the Euphorbia which grow in Mexico and the southern United States (Mills and White, 1987). The wax which coats the stems is obtained by boiling the plants in water and skimming the wax off the surface. The product is a brownish liquid which is poured into moulds to solidify, and is then broken up (Tooley, 1971).

The wax is used in conservation to harden other waxes without increasing the melting point (Mills and White, 1987).

Composition

The composition of candelilla wax (Table 4.4) has been found by gas chromatography to be 41% hydrocarbons, 8% free acids, 4% free alcohols and 6% monoesters. After methylation, the composition was found to be primarily acids and alcohols. The non-hydrocarbon content increased by 50% after methylation which is thought to be due to acids and alcohols present in the nonvolatile fraction (Tulloch, 1973). The original nonvolatile portion was 37% and is thought to contain triterpenoid esters (Mills and White, 1987).

Identification of standard spectrum

The spectrum of candelilla wax (Figure 4.7) from Euphorbia cerifera contains a shoulder centred near 3350 cm^{-1} which may be due to the O-H groups in the alcohol component. The spectrum exhibits bands at 2927 cm^{-1} and 2852 cm^{-1} which result from C-H stretching absorptions and bands at 1469 and 1381 cm^{-1} which are due to C-H deformations. The spectrum is also characterized by an absorption at 724 cm^{-1} which results from a rocking vibration of long aliphatic chains (Bellamy, 1975). The spectrum also contains strong evidence of the ester functional group with bands at 1736 and 1173 cm^{-1}. There is a second band of almost equal intensity in the carbonyl region (1714 cm^{-1}) which may be due to unionized carboxyl groups in the material. There are no distinct bands in the region 1330 - 1190 cm^{-1}, but a shoulder is observed which may be due to overlapping of bands in the region. There are weak bands at 1645 and 1606 cm^{-1} which may indicate the presence of aromatic compounds, but there is no evidence of an absorption in the region of 1515 cm^{-1}. The frequency values and band assignments for candelilla wax are listed in Table 4.6.

Paraffin wax

Source

Paraffin wax is obtained the distillation of petroleum, giving various grades which have melting point ranges between 52 and 57 °C.

Composition

Paraffin wax is composed entirely of hydrocarbons, most of which are long chain saturated compounds. The higher molecular weight fractions in paraffin have a tendency to crystallize out as very small crystals. This material is used to produce microcrystalline waxes (Mills and White, 1987).

Interpretation of standard spectra

The identification of pure paraffin wax is not difficult with infrared spectroscopy. The spectrum of the material is very simple as there is no oxygen in the structure. The spectrum shown in the literature (Kuhn, 1960) contains four absorptions at 2850, 1480, 1388 and 719 cm^{-1}. The sample spectra obtained in this study were very similar. A sample spectrum is given in Figure 4.8a and the observed frequency ranges are listed in Table 4.7. Difficulties in identification of paraffin wax arise when

it in a mixture with other, more complex materials which make the spectrum more complicated and mask the presence of the mineral wax.

The paraffin wax spectra exhibit four bands in the regions of 2960 - 2961, 2935 - 2936, 2860 and 2833 - 2837 cm^{-1} which are characteristic of C-H stretching vibrations. The spectra also contain bands at 1471 - 1472 cm^{-1} and 1379 cm^{-1} which are due to C-H deformations. The band located at 727 - 728 cm^{-1} is the result of the rocking vibration of long aliphatic chains of 4 or more methylene units. The spectrum of commercial microcrystalline wax is very similar and contains bands at 2932, 2902, 2855, 1464, 1378 and 729 cm^{-1}.

Identification of unknown samples

A sample (MF2) was removed from a the coating of a modern, bronze cast figure of a cello player (Fitzwilliam Museum). The piece was suffering from corrosion in which white salts were appearing in sheltered areas. The surface was thought to have been varnished and then waxed and the salts seem to be coming up through the wax. The sample of the waxy coating was rubbed onto the silicon carbide paper and the resulting spectrum shows some

evidence of specular reflectance as some of the strong absorptions come up past the base line of the spectrum (Figure 4.8b). However, it is still recognizable as paraffin wax as it is a simple spectrum with absorptions at 2936, 2860, 1475, 1378 and 732 cm^{-1} which are characteristic of paraffin wax (Table 4.7). There is a doublet at 1197 and 1142 cm^{-1} which is not characteristic of paraffin wax, but may result from minor impurities. These bands have been observed in some of the other reference spectra of commercial paraffin wax. There is no evidence in the spectra of the presence of varnish.

A spectrum was measured of a sample (MFA17) taken from the back of a model mummy mask (Boston Museum of Fine Arts 23-11-453/4). The sample was rubbed onto the silicon carbide paper and the diffuse reflectance spectrum was obtained. The spectrum (Figure 4.9a) contains strong bands at 2935, 2859, 1470, 1378 and 724 cm^{-1} (Table 4.7). The spectrum also contains broad bands of weaker intensity with maximum intensity at 1721, 1647, 1109, 1044 and a very weak absorption at 891 cm^{-1}. This spectrum indicated a paraffin wax mixture. The sample was also examined with the infrared microscope and found to have two distinct areas, a transparent area and a dark yellow area. The spectrum of the

white area alone was the distinctive simple one of paraffin wax. The spectrum of the yellow area contained the bands due to paraffin and other absorptions and the spectrum resembled that of the diffuse reflectance spectrum of the entire sample. The microscope investigation suggests that the paraffin and the yellow material are in layers. The yellow material has not been identified.

Spectral subtraction was utilized with the diffuse reflectance spectrum of sample MFA17 (Figure 4.9a). A diffuse reflectance spectrum of paraffin wax (BM20) was subtracted from the sample spectrum. The resulting difference spectrum, shown in Figure 4.9b, is not immediately suggestive of a particular class of compound. However, the rounded band centred at 3384 cm^{-1}, the weak band at 2122 cm^{-1}, the broad absorption at 1647 cm^{-1}, the broad band with maximum intensities at 1109 and 1040 cm^{-1} and the weak band at 912 cm^{-1} are suggestive of a gum or gum resin (see Chapter 7).

A sample (MFA12) from the back of a New Kingdom mummy mask (Boston Museum of Fine Arts 23.1475) was rubbed onto silicon carbide paper and the spectrum was obtained. The resulting

diffuse reflectance spectrum was very similar to that of sample MFA17 which was discussed above. The spectrum is marked by absorptions at 2931, 2898, 2857, 1469, 1377 and 723 cm^{-1} which are characteristic of the paraffin wax. The spectrum also contains a broad, rounded absorption centred at 3354 cm^{-1}, a weak absorption at 2135 cm^{-1}, a band at 1431 cm^{-1} and a broad absorption in the region 1200 - 980 cm^{-1} with maximum absorptions at 1115 and 1048 cm^{-1}. A weak band is observed at 895 cm^{-1}. These bands are characteristic of plant gums which are described in chapter 7. The paraffin wax is a later treatment as it was not available to the ancient Egyptians. The gum, however, may be ancient or modern. The similarity of this spectrum to the one of sample MFA17 indicates that it may reflect a similar early conservation treatment.

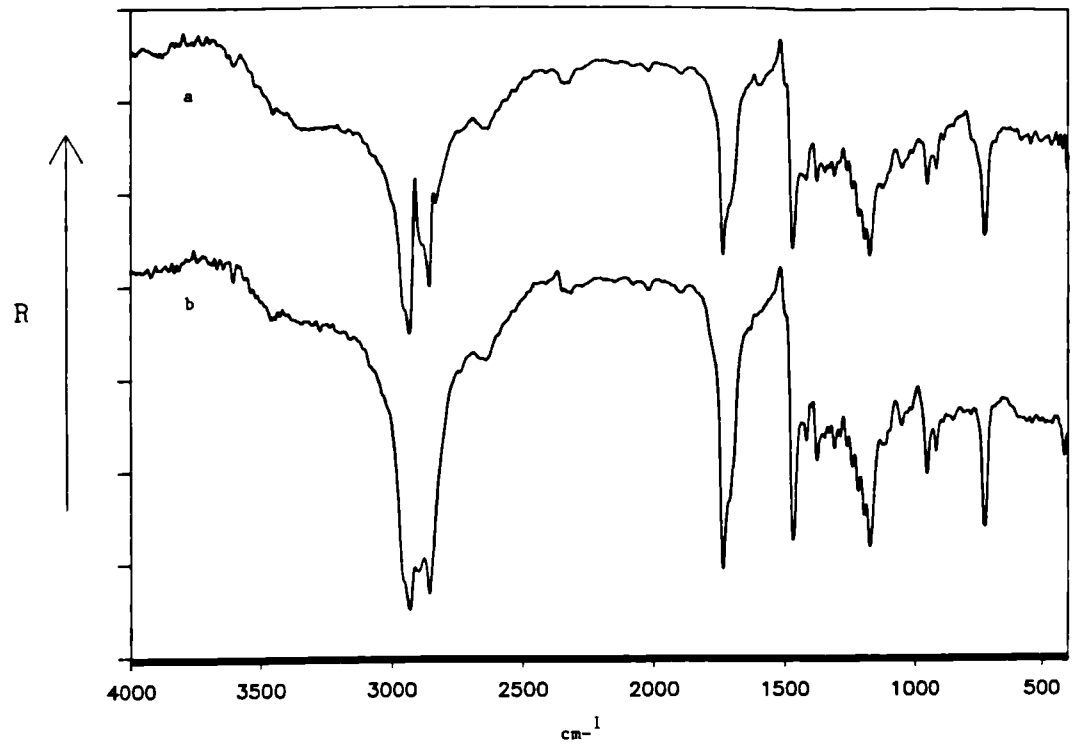


Figure 4.1 Diffuse reflectance FT-IR spectra of (a) beeswax (Apis mellifera) from an abandoned comb which was bleached in the sun (NHM19 gsva0318) and (b) a sample from an Egyptian figurine (mfa12, Boston Museum of Fine Arts 72.4783)

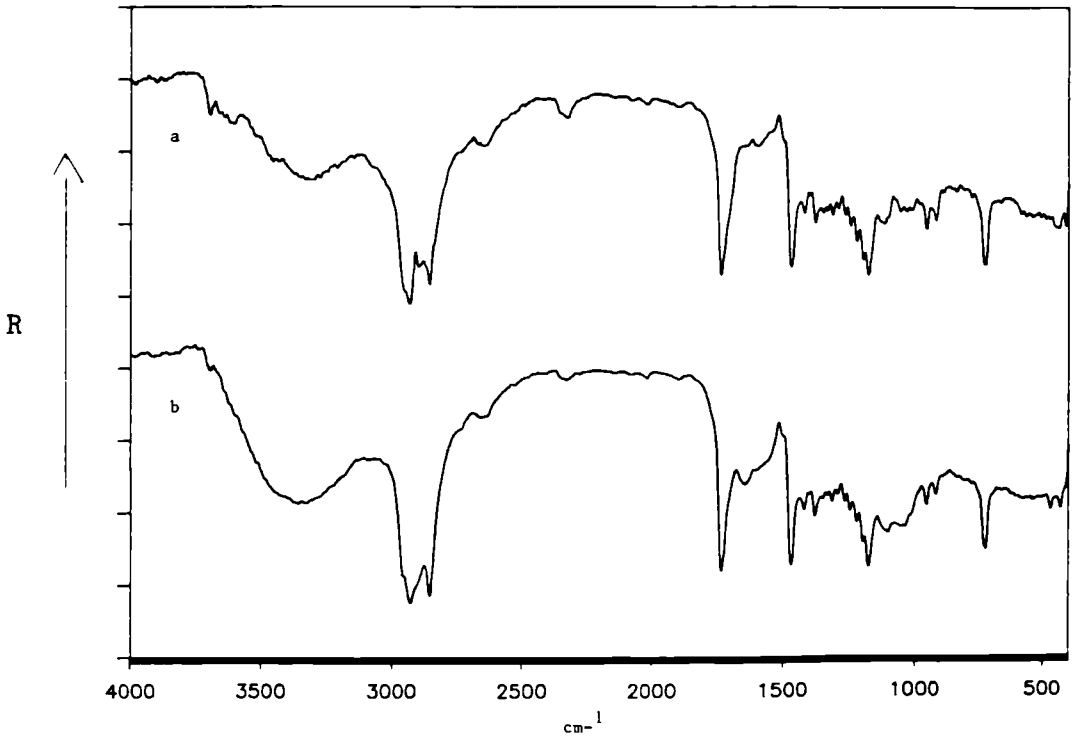


Figure 4.2 Diffuse reflectance FT-IR spectra of a wax sample (NJS8) from the site of a metal caster's workshop in Kandy, Sri Lanka, (a) interior material (gsva0233) and (b) crust (gsva0235).

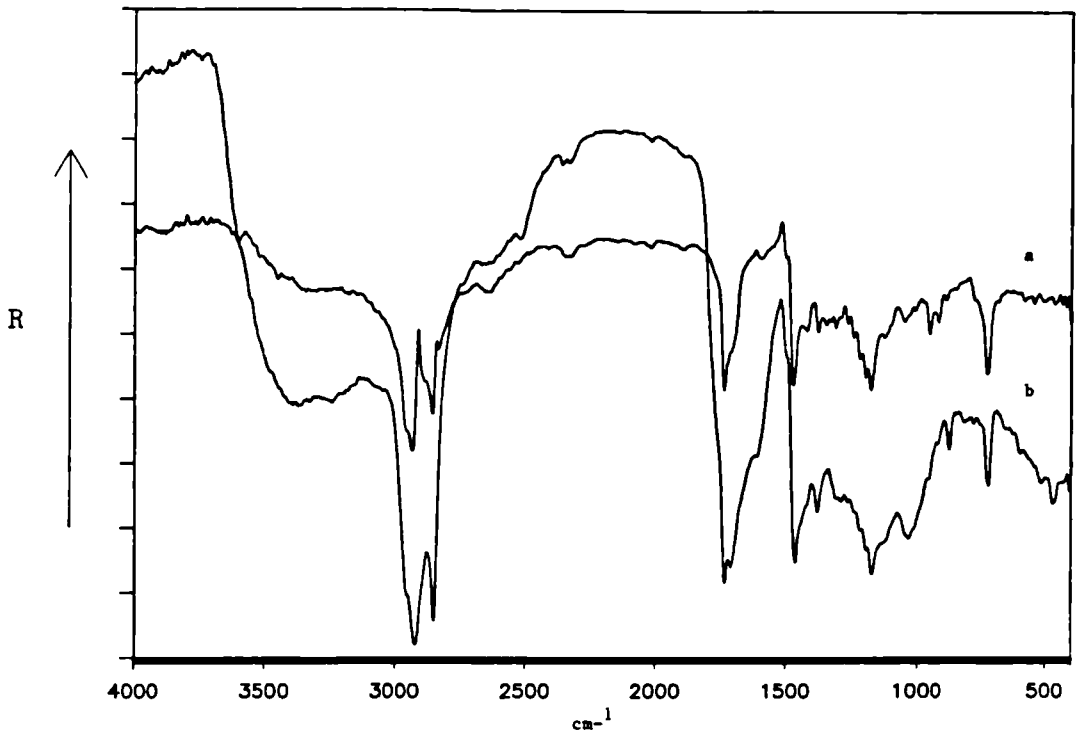


Figure 4.3 Diffuse reflectance FT-IR spectra of (a) coating sample taken from the outside of mummy Nesmin (mfa1)(Rhode Island School of Design) and (b) beeswax (Apis mellifera) (see Figure 4.1a).

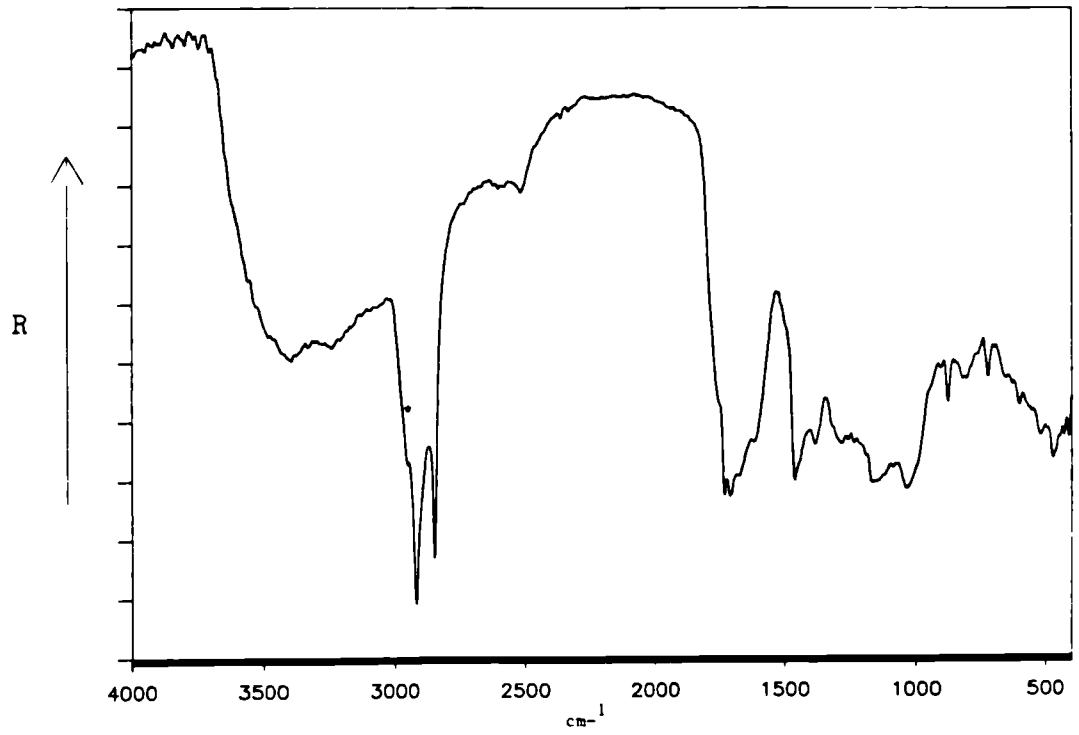


Figure 4.4 Diffuse reflectance FT-IR difference spectrum of Figure 4.3a minus Figure 4.3b obtained using interactive difference function (gsva0625).

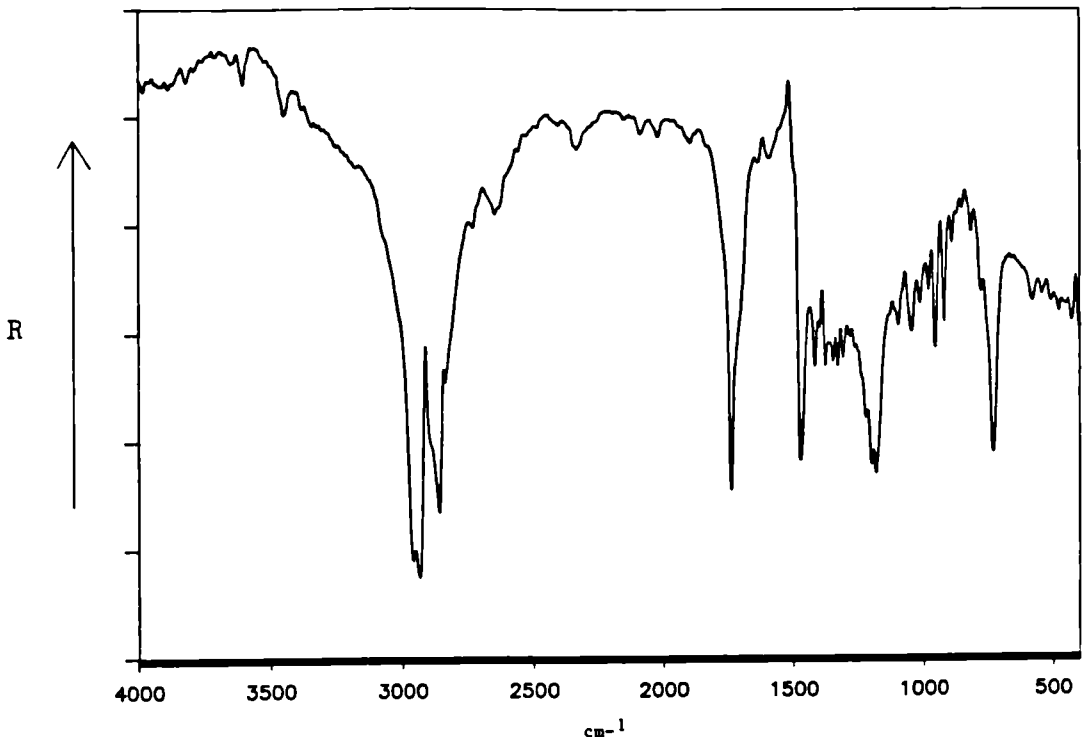


Figure 4.5 Diffuse reflectance FT-IR spectrum of spermaceti wax (BM9) (gsva0166).

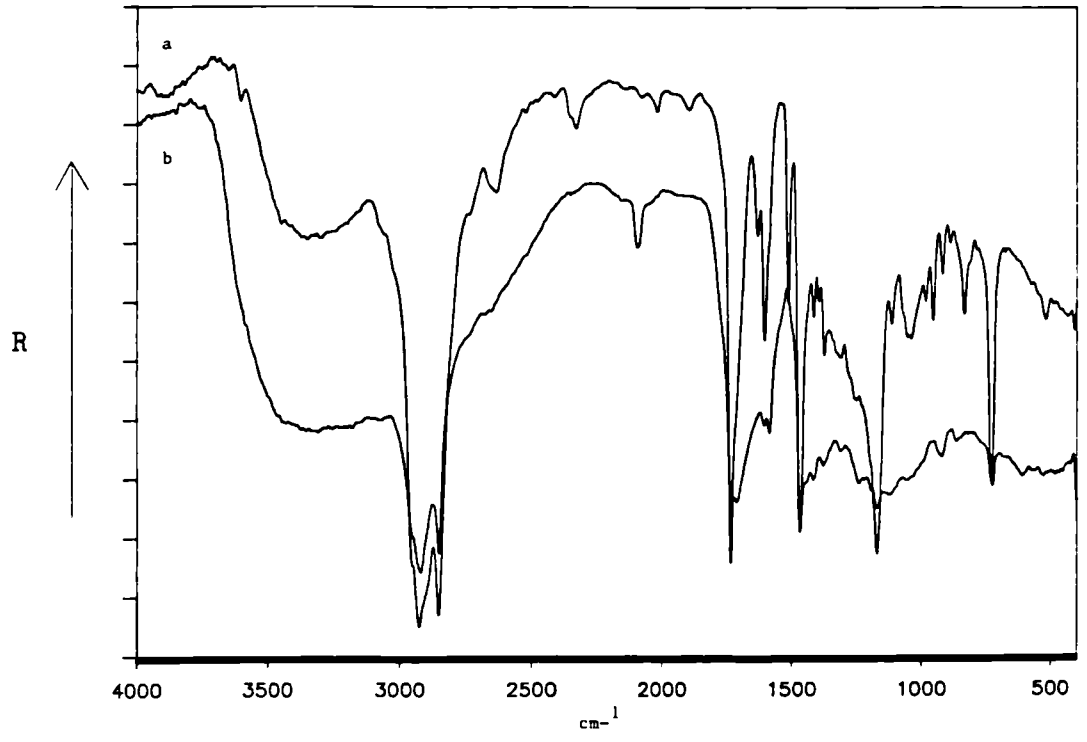


Figure 4.6 Diffuse reflectance FT-IR spectra of (a) carnauba wax (Copernicia prunifera) (Kew26 Museum of Economic Botany, Kew) (gsva0197) and (b) reconstruction material from a copper alloy vessel rim (MF4 Bedford Museum 1712) (gsva0244).

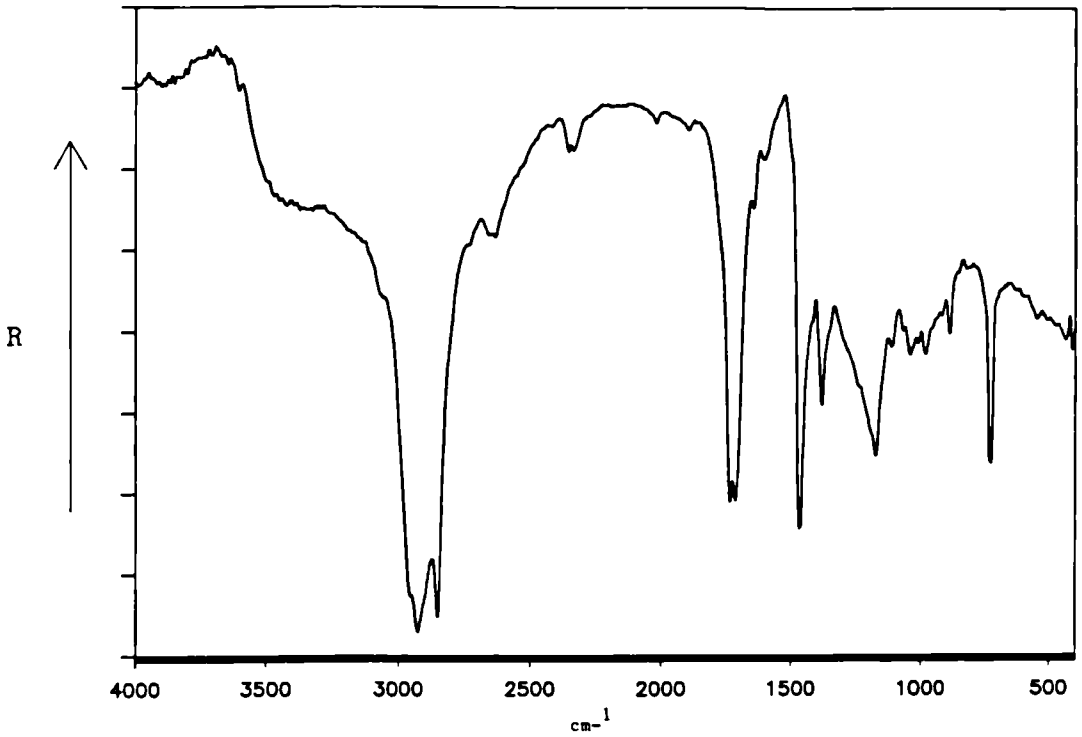


Figure 4.7 Diffuse reflectance FT-IR spectrum of candelilla wax (Euphorbia cerifera) (Kew 27, Museum of Econimic Botany, Kew) (gsva0198).

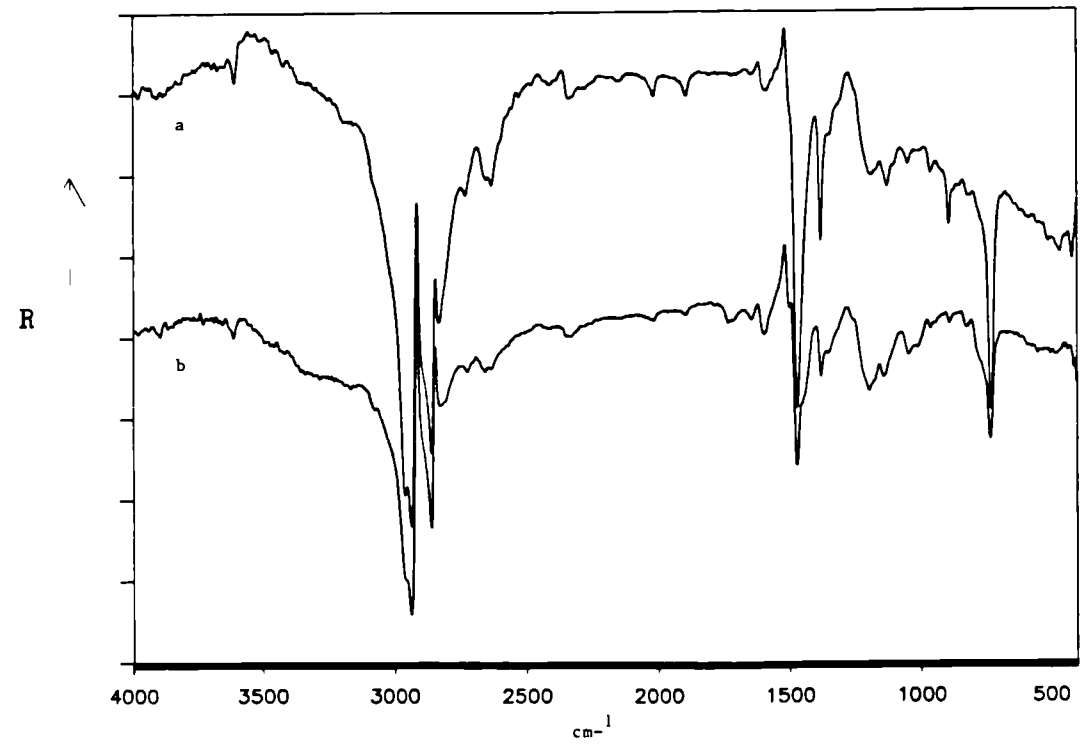


Figure 4.8 Diffuse reflectance FT-IR spectra of (a) paraffin wax (BM20 BDH) (gsva0183) and (b) wax coating from a figure of a cello player (MF2 Fitzwilliam Museum).

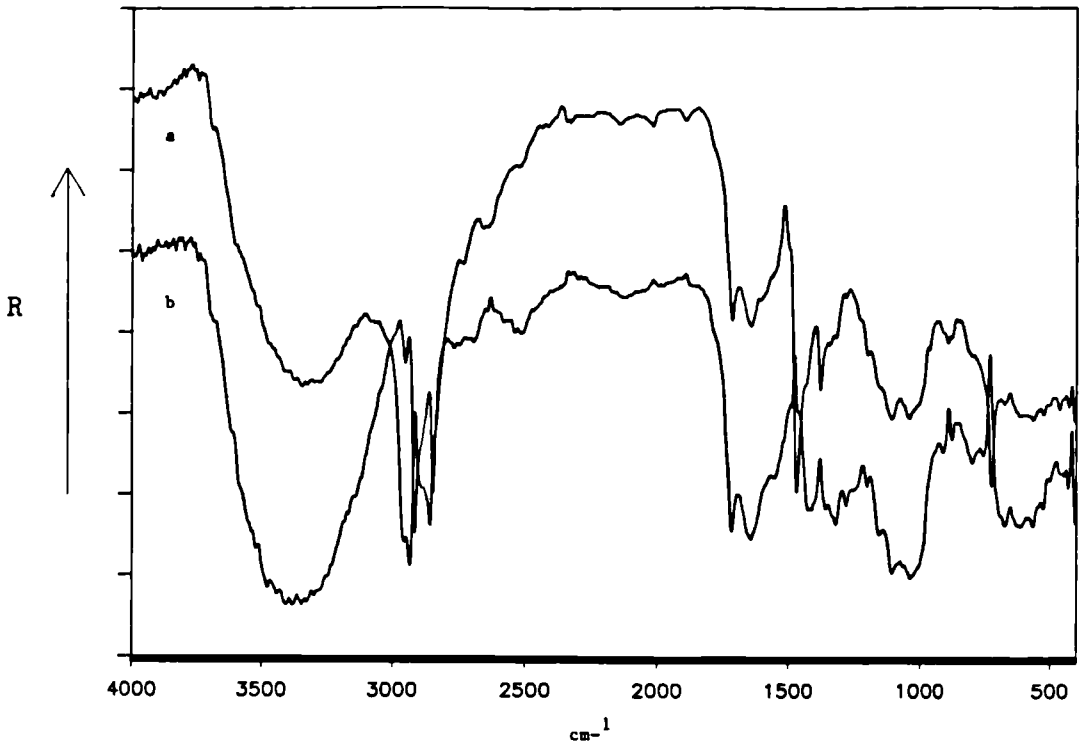


Figure 4.9 Diffuse reflectance FT-IR spectrum of (a) material from the back of a model mummy mask (mfa17, Boston Museum of Fine Arts 23-11-453/4) and (b) the difference spectrum of Figure 4.9a minus Figure 4.8a obtained using the interactive difference function.

Table 4.1

Composition of beeswax (Tulloch, 1971)

Component		Percent by weight
Hydrocarbons		14.0
Monoesters		34.7
Diesters		13.7
Triesters		3.3
Hydroxy monoesters		3.
Hydroxy polyesters		7.7
Free acids		11.9
Acid monoesters		0.8
Acid polyesters		1.7
Unidentified	Recovered from column	2.1
	Not recovered from column	6.5

Table 4.4

Composition of carnauba and candelilla waxes (Tulloch, 1973)

Components	Wax Carnauba (%)	Candelilla (%)
Hydrocarbons	--	41
Free acids	--	8
Free alcohols	11	4
Monoesters	36	6
Hydroxy esters	--	--
Unidentified *	--	6(2)
Total volatile	47	65

* Number of components in parentheses.

TABLE 4.2

Frequency values and band assignments for beeswax and unknowns identified as beeswax

Reference samples	Trigona sample	Unknown samples beeswax	Unknown samples mixtures	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1			cm-1	
3345 - 3310(sh)	3435(m)	3461 - 3277(sh)	3375 - 3323(m)	O-H stretch	alcohol	3450	1
2935 - 2932(s)	2921(s)	2933 - 2924(s)	2935 - 2922(s)	C-H stretch	methyl, methylene and methine groups	2850	1
				C-H stretch	methylene groups	2926 ± 10(s)	2
* 2904 - 2894(va)		2904 - 2899(va)		C-H stretch	methine groups	2890 ± 10(w)	2
2859 - 2856(s)	2851(s)	2857 - 2852(s)	2860 - 2852(s)	C-H stretch	methylene groups	2853 ± 10(s)	2
1741 - 1736(s)	1735(s)	1739 - 1737(s)	1739 - 1736(s)	C=O stretch	ester	1730	1
				C=O stretch	ester	1750 - 1730(s)	2
** nr 1710(vw sh)	near 1710(sh)	** nr 1710(vw sh)	**1713(s)	C=O stretch	carboxylic acids non-ionized	1709	1
				C=O stretch	carboxylic acids non-ionized	1725 - 1700(s)	2
1474 - 1470(s)	1463(s)	1472 - 1470(s)	1477 - 1464(s)	C-H deformation	methyl and methylene groups	1470	1
				C-H asym. deformation	methyl groups	1450 ± 20(m)	2
				C-H deformation	methylene groups	1465 ± 20(m)	2
1420 - 1418(w)	near 1420(w)	1420 - 1418(w)		C-H deformation	methylene group next to carboxylic acid	1410 - 1405	4,5
1379 - 1377(w)	1383(s)	1378 - 1377(w)	1379 - 1377(w)	C-H deformation	methyl groups	1388	1
				C-H sym. deformation	methyl groups	1380 - 1370(s)	2

TABLE 4.2 contd.

Frequency values and band assignments for beeswax and unknowns identified as beeswax

Reference samples	Trigona sample	Unknown samples beeswax	Unknown samples mixtures	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1			cm-1	
near 1347(w)		* 1348 - 1347(w)		unassigned	solid samples	1333 - 1190	1
1331 - 1330(w)		1332 - 1331(w)	1325 - 1312(w)	C-H 'wagging and	methylene groups	1350 - 1180	
1312 - 1311(w)	near 1285(sh)	1292 - 1290(w)	1291 - 1290(w)	twisting'vibrations	in fatty acids	band progression	3
near 1267(w)		1267 - 1266(w)	near 1266(sh)			series of weak	
1246 - 1245(w)	near 1240(sh)	1246 - 1244(w)	near 1244(sh)			evenly spaced bands	
near 1221(w)		1221 - 1220(w)	near 1220(sh)				
1198 - 1197(w)		1198 - 1197(w)	near 1197(sh)				
1179 - 1176(s)	1176(s)	1178 - 1176(s)	1176 - 1173(s)	C-O stretch	ester	1177	1
				C-O stretch	ester	1200 - 1150(s)	2
1056 - 1053(w)	1046(m)	1055 - 1052(va)	1052 - 1036(va)	unassigned			
959 - 958(m)	near 965(vw)	959 - 957(m)	* 958(va)	unassigned	solid samples	962	1
922 - 921(m)	near 925(vw)	922 - 920(m)	* 920(va)	unassigned	solid samples	918	1
891 - 866(w)	near 890(sh)			unassigned	solid samples	890	1
729 - 722(s)	724(s)	726 - 723(s)	729 - 722(s)	chain vibration	long chain	730	1
					hydrocarbons	719	1
				chain rocking vibration	long chain hydrocarbons with four or more methylene groups	750 - 720(m)	2

* Absorption is weak or occurs as a shoulder in some spectra.

** Absorption is not apparent in some spectra.

1. Kuhn, 1960
2. Bellamy, 1975
3. Jones et al., 1952
4. Sinclair et al., 1952a
5. Sinclair et al., 1952b

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 4.3

Frequency values and band assignments for spermaceti wax

Spermaceti wax cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
near 3450(vw sh)	O-H stretch	alcohol (polymeric)	3400 - 3200(vs,b) hydrogen bonded	1
		carboxylic acid hydrogen bonded	3000 - 2500(b)	1
2960(s)	C-H stretch	methyl group	2962 ± 10(s)	1
2935(s)	C-H stretch	methylene group	2926 ± 10(s)	1
2860(s)	C-H stretch	methyl group	2872 ± 10(s)	1
		methylene group	2853 ± 10(s)	1
2838(s)	C-H stretch	methylene group	2853 ± 10(s)	1
2650(w)	O-H stretch	carboxylic acid hydrogen bonded	near 2650(w)	1
1741(s)	C=O stretch	ester	1750 - 1730(s)	1
near 1700(sh)	C=O stretch	carboxylic acid	1725 - 1700(s)	1
1474(s)	C-H asym. deformation	methyl group	1450 ± 20(m)	1
	C-H deformation	methylene group	1465 ± 20(m)	1
1418(w)	C-O stretch or O-H deformation	carboxylic acid	1440 - 1395(w)	1
1378(w)	C-H sym. deformation	methyl group	1380 - 1370(s)	1
1348(w)	C-H 'wagging and	methylene groups	1350 - 1180	2
1330(w)	twisting' vibrations	in fatty acids	band progression	
1309(w)			series of weak	
1284(w)			evenly spaced bands	
1223(w)				
1202(s)				
1184(s)	C-O stretch	ester	1200 - 1150(s)	1
1099(w)	unassigned			
1048(w)	unassigned			
984(w)	unassigned			
958(m)	unassigned			
922(m)	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)	1
890(w)	unassigned			
851(w)	unassigned			
816(w)	unassigned			
776(w)	unassigned			
730(s)	chain rocking vibration	long chain hydrocarbon with four or more methylene units	750 - 720(m)	1

1. Bellamy, 1975
2. Jones et al., 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; s

TABLE 4.5

Frequency values and band assignments for carnauba wax and unknown sample identified as carnauba wax

VA1 cm-1	BM22 cm-1	Kew26 cm-1	MF4 unknown cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
3337(m,b)	3354(m,b)	3353(m,b)	3341(m,sh)	O-H stretch	alcohol (polymeric)	3400 - 3200(vs,b) hydrogen bonded	1
				O-H stretch	carboxylic acid	3000 - 2500(b)	1
2927(s)	2925(s)	2927(s)	2922(s)	C-H stretch	methylene group	2926 ± 10(s)	1
2852(s)	2852(s)	2853(s)	2852(s)	C-H stretch	methylene group	2853 ± 10(s)	1
2642(w)	2641(w)	2637(w)	near 2600(vwsh)	O-H stretch	carboxylic acid	near 2650(w)	1
1737(s)	1736(s)	1736(s)	1734(s)	C=O stretch	ester	1750 - 1730(s)	1
near 1700(sh)	near 1700(sh)	near 1700(sh)	1713(s)	C=O stretch	carboxylic acid	1725 - 1700(s)	1
1633(w)	1633(w)	1633(w)		skeletal ring stretch	aromatic ring	1625 - 1575(va)	1
1607(m)	1606(s)	1606(s)	1608(w)	skeletal ring stretch	aromatic ring	1600 - 1560(w unless conjugated)	1
			1588(w)	skeletal ring stretch	aromatic ring	1612	2
1516(m)	1516(s)	1516(s)		skeletal ring stretch	aromatic ring	1525 - 1475(va)	1
						1515	2
1470(s)	1470(s)	1470(s)	1469(s)	C-H asym. deformation	methyl group	1450 ± 20(m)	1
				C-H deformation	methylene group	1465 ± 20(m)	1
1417(w)	1417(w)	1417(w)	1419(w)	C-O stretch or O-H deformation	carboxylic acid	1440 - 1395(w)	1
1397(vw)	1396(w)	1397(w)		unassigned			
1376(w)	1376(w)	1376(w)	1379(w)	C-H sym. deformation	methyl group	1380 - 1370(s)	1
1316(w)	1316(w)	1310(w)	1312(w)	unassigned			
			1243(w)	unassigned			
1174(s)	1173(s)	1173(s)	1174(s)	C-O stretch	ester	1200 - 1150(s)	1

(TABLE 4.4 see page 202)

TABLE 4.5 contd.

Frequency values and band assignments for carnauba wax and unknown sample identified as carnauba wax

VA1 cm-1	BM22 cm-1	Kew26 cm-1	MF4 unknown cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
1115(w)	1114(w)	1115(w)		unassigned			
1040(m)	1040(m)	1041(m)		unassigned			
957(m)	957(m)	957(m)		unassigned			
921(w)	922(w)	921(w)	924(w)	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)	1
888(w)	888(w)	889(w)	864(w)	C-H out-of-plane deformation	aromatic ring	900 - 860(m) one free H atom	1
833(m)	832(m)	832(m)		C-H out-of-plane deformation	aromatic ring	860 - 800(vs) para-substitution	1
				C-H out-of-plane deformation	aromatic ring	833	2
724(s)	724(s)	724(s)	722(s)	chain rocking vibration	long chain hydrocarbons with four or more methylene units	750 - 720(m)	1

1. Bellamy, 1975
2. Kuhn, 1960

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 4.6

Frequency values and band assignments for candelilla wax

Kew27 cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
near 3350(m sh)	O-H stretch	alcohol (polymeric)	3400 - 3200(vs,b) hydrogen bonded
	O-H stretch	carboxylic acid hydrogen bonded	3000 - 2500(b)
2927(s)	C-H stretch	methylene group	2926 ± 10(s)
2852(s)	C-H stretch	methylene group	2853 ± 10(s)
2636(w)	O-H stretch	carboxylic acid hydrogen bonded	near 2650(w)
1736(s)	C=O stretch	ester	1750 - 1730(s)
1714(s)	C=O stretch	carboxylic acid	1725 - 1700(s)
1645(s)	skeletal ring stretch	aromatic ring	1625 - 1575(va)
1606(w)	skeletal ring stretch	aromatic ring	1600 - 1560(w unless conjugated)
1469(s)	C-H asym. deformation	methyl group	1450 ± 20(m)
	C-H deformation	methylene group	1465 ± 20(m)
near 1400(w sh)	C-O stretch or O-H deformation	carboxylic acid	1440 - 1395(w)
1381(s)	C-H sym. deformation	methyl group	1380 - 1370(s)
1173(s)	C-O stretch	ester	1200 - 1150(s)
1112(w)	unassigned		
1042(w)	unassigned		
985(w)	unassigned		
near 900(vw)	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)
885(w)	C-H out-of-plane deformation	aromatic ring	900 - 860(m) one free H atom
near 830(vw)	C-H out-of-plane deformation	aromatic ring	860 - 800(vs) para-substitution
724(s)	chain rocking vibration	long chain hydrocarbon with four or more methylene units	750 - 720(m)

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 4.7

Frequency values and band assignments for paraffin wax and samples identified as paraffin wax

Paraffin wax cm-1	Micro-crytal-line wax cm-1	Unknown MF2 cm-1	Unknown MFA12 cm-1	Unknown MFA17 cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
2961 - 2960(s)					C-H stretch	methyl group	2962 ± 10(s)
2936 - 2935(s)	2932(s)	2936(s)	2931(s)	2935(s)	C-H stretch	methylene group	2926 ± 10(s)
	2902(s)		2898(s)		C-H stretch	methine group	2890 ± 10(w)
2860(s)	2855(s)	2860(s)	2857(s)	2859(s)	C-H stretch	methyl group	2872 ± 10(s)
2837 - 2833(s)					C-H stretch	methylene group	2853 ± 10(s)
1472 - 1471(s)	1464(s)	1475(s)	1469(s)	1470(s)	C-H asym. deformation	methyl group	1450 ± 20(m)
					C-H deformation	methylene group	1465 ± 20(m)
1379(s)	1378(s)	1378(m)	1377(m)	1378(m)	C-H sym. deformation	methyl group	1380 -1370(s)
728 - 727(s)	729(s)	732(s)	723(s)	724(s)	chain rocking vibration	long chain hydro-carbon with four or more methylene units	750 - 720(m)

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

CHAPTER 5 FATS AND OILS

Source

Fats are classified as lipids (Tooley, 1971). Fats have been utilized by man since early times and sources include animal fat tissue (tallow) and various vegetable sources such as olives and nuts (Mills and White, 1987; Tooley, 1971).

Composition

Unaltered fats and oils

True fats or glyceryl esters of fatty acids are the principle components of fats and oils. Fatty acids are long chain carboxylic acids. Some fatty acids are completely saturated which means there are no C=C bonds in the structure and some other structures contain one or more double bonds. The structure of glycerol is given in Figure 5.1a. It is an alcohol with three hydroxyl groups (trihydric) and it may be mono-, di- or tri-substituted with fatty acids containing one carboxyl group. Fats and oils which have not undergone degradation contain tri-substituted esters only. The triglycerides may be substituted with the same kind of fatty acid. These materials are refered to as simple triglycerides (Figure 5.1b). However, most triglycerides from natural sources are mixed glycerides or esters

with more than one type of fatty acid substituent. Oils are similar in basic structure, but are liquids at room temperature. The melting point is affected by the molecular weight of the fatty acids and the degree of saturation. For example, fats from vegetable sources are composed mainly of unsaturated fatty acids and have lower melting points than animal fat which consists primarily of saturated fatty acids (Tooley, 1971; Mills and White, 1987).

The majority of fatty acid esters are composed of only a few of the large number of fatty acids which are known to occur in fats. The important fatty acids are stearic, oleic and the other compounds composed of 18 carbon atoms. The common fatty acids are listed in Table 5.1. Natural products are made up of mixtures of the various triglycerides. The structures are very complex and have not been fully elucidated. Gas chromatography is not ideal as the triglycerides have a high molecular weight and low volatility. Most analyses are based on the fatty acid content which may be measured after the saponification or hydrolysis of the ester linkages. The composition for each type of oil is variable and is affected by such factors as the species of plant, soil environment and the climatic conditions. A table

(Table 5.2) (Mills and White, 1987) has been compiled of the ranges of fatty acid composition which have been obtained using gas chromatography which is the most reliable method. As mentioned earlier, only a few important fatty acid structures are incorporated into the structures and the differentiations are based on quantitative measurements (Mills and White, 1987).

Effects of ageing

The ester linkages in fats and oils are susceptible to cleavage. The mechanism is the hydrolysis of the bonds which produces glycerol and free fatty acids. Archaeological specimens of fat or oils have often been found to consist entirely of the free fatty acids. The glycerol seems to be removed by water. The reaction may be caused by water over a long period of time although it may also be due to bacteria (Mills and White, 1987).

Identification and interpretation of standard spectra

Standard sample information

The principal method of analysis for fats is gas chromatography of the fatty acid content after hydrolysis or saponification of the ester linkages and methylation of the esters. The great similarity in composition of the materials makes their

differentiation by infrared spectroscopy unlikely. For this thesis, transmission spectra of two types of olive oil and four kinds of seed oil were measured at high resolution (2 cm^{-1}) to determine if any differentiation might be made. A sample of lamb suet was analyzed as a solid utilizing diffuse reflectance spectroscopy. The fat was not examined until two weeks after it was obtained and although it was kept refrigerated, there is some evidence of decomposition in the spectrum. This is not unexpected and it was desirable to obtain the spectrum of degradation products as that is what is examined in archaeological specimens. Also, spectra were obtained of four fatty acids: oleic (transmission), myristic, palmitic and stearic acids (diffuse reflectance).

Vegetable and seed oils

The spectra of the six oils were found to be extremely similar (Figure 5.2). Only very minor variations are visible in the region 1150 - 800 cm^{-1}. In the spectra of safflower oil (GS10), grapeseed oil (GS11) and walnut oil (GS12), there is a relatively weak band at 1100 cm^{-1} with a less intense band which occurs in the region of 1120 cm^{-1} as a shoulder on the strong band at 1163 - 1164 cm^{-1}. The band near 1120 cm^{-1} is slightly more intense

than the band at 1100 cm^{-1} in the spectra of the two olive oils (GS9 and GS14) and the hazelnut oil (GS13). There is a minor band in the region of 915 cm^{-1} in the spectra of the safflower, grapeseed and walnut oils which is not apparent in the other three materials.

The remaining bands in the spectra may be assigned to characteristic groups in triglycerides (Table 5.3). The spectra are characterized by bands in the regions of 2926 - 2925 cm^{-1} (with a shoulder in the region of 2954 cm^{-1}), 2855 - 2854 cm^{-1}, 1466 and 1378 cm^{-1} which are indicative of C-H stretching and bending vibrations. The values listed in the literature (Sinclair et al., 1952a) for saturated and monounsaturated fatty acids are 2920 and 2850 cm^{-1} assigned to the C-H stretches in methylene groups with weaker bands near 2960 and 2870 cm^{-1} which are assigned to the methyl group absorptions. The intensity of the methyl group bands increases in relation to those of the methylene groups in the spectra of materials with higher numbers of double bonds. The band in the region of 2870 cm^{-1} is not evident in the spectra of the vegetable oils. The spectra of the oils are also marked by absorptions in the range 724 - 723 cm^{-1} which correspond to values quoted in the literature for the

rocking vibration which occurs in aliphatic hydrocarbon chains longer than four units, 750 - 720 cm^{-1} (Bellamy, 1975). The values of 720 cm^{-1} (Sinclair et al., 1952a; Sinclair et al., 1952b) and 719 cm^{-1} (Shreve et al., 1950) have been given for the fatty acids, methyl esters of fatty acids and the triglycerides which were studied.

The spectra of unsaturated materials exhibit characteristic absorptions which are due to the double bond. The regions include the ethylenic C-H stretch which falls in the area 3100 - 3000 cm^{-1}, the C=C stretch which absorbs in the region 1580 - 1650 cm^{-1} and the out-of-plane deformations of the =C-H bond which occur in the regions near 980 and 690 cm^{-1} (Sinclair et al., 1952b). The oil standard spectra are characterized by absorptions in the region 3009 - 3005 cm^{-1} which are assigned to the C-H stretch on the double bond carbons. The values given in the literature for fatty acids are 3020 cm^{-1} (Sinclair et al., 1952b) and near 3030 cm^{-1} (Shreve et al., 1950). The spectra of the oils contain a very weak absorption in the region 1657 - 1656 cm^{-1} and several contain a second weak band at 1650 cm^{-1}. These bands may be representative of the C=C stretches, but, there is evidence of water in the spectra which is thought to be

from the KBr plates used to hold the sample and it is difficult to say whether the bands are due to water or the sample. The literature reports that the band attributed to the C=C bond occurs as an unresolved shoulder at 1660 cm^{-1} which occurs on the band near 1708 cm^{-1} in the spectra of unsaturated fatty acids (Sinclair et al., 1952b). There are no strong bands in the region 980 - 690 cm^{-1} except for the band in the region of 723 cm^{-1}. However, the band near 723 cm^{-1} exhibits a broad shoulder on the right side which ends around 670 cm^{-1}. This may correspond to the presence of a cis-substituted double bond structure. Trans-substituted unsaturated fatty acids are characterized by a fairly strong absorption in the region 980 - 965 cm^{-1} (Sinclair et al., 1952b) and small amounts of trans-structures may result in a weak band in this region. A very weak band is observed near 970 cm^{-1} in the spectra of the vegetable oils. Unsaturated structures also effect the region between 1460 - 1400 cm^{-1}. The literature reports the presence of a band in the region of 1405 - 1410 cm^{-1} in both saturated and unsaturated fatty acids which is thought to be due to the methylene group next to the carboxyl functional group (Sinclair et al., 1952a; Sinclair et al., 1952b). A second band which is attributed to

the methylene group in the immediate vicinity of the C=C bond is located in the region of 1435 cm^{-1} in the unsaturated fatty acid spectra (Sinclair et al., 1952a). The intensity of the band was observed to increase as the number of double bonds increase. The vegetable oils, which are predominantly composed of triglycerides, have ester functional groups instead of carboxyl groups which may result in the appearance of the band in the region of 1405 - 1410 cm^{-1}. In the oil spectra, two very weak bands occur in the region of 1430 cm^{-1} which occurs as a shoulder on the band at 1466 cm^{-1} and near 1417 cm^{-1}.

The spectra of the vegetable oils are characterized by bands which result from the ester linkages. The frequencies of several triglycerides have been reported (Shreve et al., 1950). The values for the C=O stretch fall into the range 1751 - 1748 cm^{-1}. The region 1250 - 1100 cm^{-1} is characteristic of triglycerides and thought to be related to the C-O stretching vibration in the ester functional group. The region is marked by a strong absorption near 1163 cm^{-1} with less intense absorptions near 1250 and 1111 cm^{-1}. In the spectra which are presented (Shreve et al., 1950), those of the unsaturated tri-elaidon and tri-olein exhibited patterns which consist of a strong band near 1163 cm^{-1}

and one at 1236 and 1239 cm^{-1} respectively. However, instead of one absorption at 1111 cm^{-1} which is evident in the two spectra of the triglycerides composed of saturated fatty acids (trimyristin and tripalmitostearin), the spectra of the trielaidon and tri-olein exhibit two bands at 1121 cm^{-1} and 1101 - 1099 cm^{-1} (Shreve et al., 1950). This pattern is evident in the spectra of the oils examined in this thesis where bands occur in the ranges 1239 - 1238 cm^{-1}, 1164 - 1163 cm^{-1}, 1100 - 1097 cm^{-1} and a band in the region 1120 - 1119 cm^{-1} which is very weak in three of the spectra which were discussed earlier. The oil spectra also exhibit a very strong band in the region of 1747 - 1746 cm^{-1} which is only slightly beyond that given in the literature for triglycerides (Shreve et al., 1950).

Lamb suet

The spectrum of the lamb suet (Figure 5.3) is marked by absorptions at 2940 cm^{-1} with a shoulder in the region of 2960 cm^{-1} and absorptions at 2862 and 2835 cm^{-1} with a shoulder on the band at 2862 cm^{-1} which may represent the band expected at 2870 cm^{-1}. These bands are due to the C-H stretching vibrations. The spectrum also exhibits bands 1471 cm^{-1} and 1379 cm^{-1} which result from C-H deformation vibrations. The spectrum also contains a

band at 727 cm^{-1} which is the result of aliphatic chain rocking vibration. The only major variation between this spectrum and those of the oils is that the bands due to the methyl group C-H stretches, the shoulders near 2960 cm^{-1} and 2870 cm^{-1}, are more pronounced. The frequency values are given with the band assignments in Table 5.3.

Although animal fats are composed predominantly of saturated fatty acid esters, they contain a certain amount of unsaturated material. Mutton tallow has been found to contain 30% oleic acid and 1.5% linoleic acid (Mills and White, 1987). The spectrum of the lamb suet exhibits certain bands which may be assigned to the double bond structure. A weak shoulder appears in the region of 3010 cm^{-1} which probably corresponds to the ethylenic C-H stretch which has been reported to fall near 3020 - 3030 cm^{-1} (Sinclair et al., 1952b; Shreve et al., 1950). The spectrum also exhibits a band at 1654 cm^{-1} which is of greater relative intensity than those in the oil spectra and is probably due to the C=C stretch. The band at 964 cm^{-1} is of medium intensity in relation to the other bands in the spectrum and falls into the range given for trans-isomer structures, 980 - 965 cm^{-1} (Sinclair et al., 1952b). There is no strong evidence for a cis-isomer structure: a very

weak shoulder appears from approximately 710 to 670 cm^{-1} which may indicate traces of cis-substituted materials. The range reported for cis-isomers is near 690 cm^{-1} (Sinclair et al., 1952b). Also, a weak band appears at 1418 cm^{-1} in the suet spectrum which corresponds to the weak bands observed near 1417 cm^{-1} in the oil spectra and are probably due to the C-H deformations of the methylene groups which are adjacent to the carboxyl group. The band at 1471 cm^{-1} has a shoulder in the region of 1445 cm^{-1} which may be due to the methylene groups in the immediate vicinity of the C=C bonds which have been reported to occur in the region (Sinclair et al., 1952b).

The spectrum of the suet also contains evidence for the ester linkage. There is a very intense band at 1756 cm^{-1} and a second intense band at 1184 cm^{-1} which are due to the C=O and the C-O stretch respectively. The band is flanked by a weak absorption at 1121 cm^{-1}, but the band which is expected near 1239 cm^{-1} is not apparent. A wide shoulder occurs near 1200 cm^{-1} which reaches to almost 1300 cm^{-1}.

There is some evidence for the presence of carboxylic acid functional group in the spectrum which would indicate the break

down of some of the triglyceride structure. A band appears as a shoulder on the C-H stretching absorptions with a maximum intensity at 3304 cm^{-1} and a further band occurs at 2671 cm^{-1}. These bands are representative of the O-H bond in carboxylic acids which form hydrogen bonded dimers in the solid and liquid state. The absorption has been described as a shoulder on the bands due to the C-H stretching vibration (Shreve et al., 1950; Sinclair et al., 1952a). Also, the band has been reported to occur near 2703 cm^{-1} which was assigned as "a branch of the O-H··· O 'association' band" which is part of the total O-H absorption" (Shreve et al., 1950). Bellamy (1975) refers to the band in the region 2700 - 2500 cm^{-1} as a satellite band of the bonded O-H absorption. A shoulder is observed on the band at 1756 cm^{-1} in the suet spectrum in the region of 1735 - 1680 cm^{-1} which may be due to small amounts of carboxylic groups which exhibit carbonyl stretches in the region 1701 - 1698 cm^{-1} (Sinclair et al., 1952a and 1715 - 1709 cm^{-1} (Shreve et al., 1950). Also, fatty acid spectra contain a series of evenly spaced weak bands in the region 1350 - 1180 cm^{-1} which are due to wagging and twisting vibrations of the methylene groups (Jones et al., 1952). Small amounts of fatty acids may result in the broad shoulder which is

observed in this region in the suet spectrum and mask the weak absorption expected in the region 1250 - 1238 cm^{-1}.

Fatty acids

The spectrum of oleic acid was obtained by transmission and the spectra of the saturated fatty acids were recorded using diffuse reflectance. The spectra exhibit characteristic carboxylic acid absorptions in addition to the absorptions due to aliphatic functional groups and there is no evidence of ester linkages. The major spectral frequency ranges are reported with the assignments in Table 5.4.

The oleic acid spectrum contains bands at 2925 and 2854 cm^{-1} which are due to aliphatic C-H stretching vibrations. The spectrum also exhibits absorptions at 1466 and 1378 cm^{-1} which correspond to those of aliphatic C-H deformations. The band which occurs at 723 cm^{-1} in the spectrum is due to the rocking vibration of aliphatic chains of four or more methylene groups. In addition to the aliphatic absorptions, the spectrum contains a band at 3006 cm^{-1} which may be assigned to the C-H stretches on the C=C groups. Bands appear at 1434 and 1413 cm^{-1} which may be assigned to the C-H deformations of the methylene groups adjacent

to the C=C groups and the carboxyl groups respectively (Sinclair et al., 1952b). The strong band at 1711 cm^{-1} exhibits a slight widening at base on the right hand side which may be the result of C=C stretching vibrations which have been reported to absorb weakly in the region of 1660 cm^{-1} (Sinclair et al., 1952b). Also, the band at 723 cm^{-1} has a broad shoulder in the approximate region of 705 - 660 cm^{-1} which may be indicative of the presence of cis-isomer structures (Sinclair et al., 1952b).

The presence of carboxyl groups is indicated by the band which occurs at 1711 cm^{-1} which is above the range given by Sinclair et al. (1952a), but fits within the values reported by Shreve et al. (1950), 1715 - 1709 cm^{-1}. This region has been assigned to the C=O of the carboxylic acid group and the shift from the values for the triglycerides (1751 - 1748 cm^{-1}) is diagnostic (Shreve et al., 1950). The spectrum also exhibits a slight shoulder from about 3500 - 3080 cm^{-1} which is probably the result of a combination of water from the KBr plates and the hydrogen bonded O-H stretch in the carboxyl group. The band at 2675 cm^{-1} is also diagnostic of carboxylic acids. There are two very weak bands on the shoulder of the band at 1378 cm^{-1} at 1285 and 1247 cm^{-1}. Bands have been reported near 1282 and 1250 cm^{-1} (Shreve et al.,

1950) which have tentatively been assigned to the C-O stretching vibration in the carboxyl group. The oleic acid spectrum exhibits a band of medium intensity at 939 cm^{-1} which may be assigned to the deformation of the O-H linkage in the carboxylic acid group which is reported to occur near 935 cm^{-1} (Shreve et al., 1950). There are two very weak absorptions at 1119 and 1091 cm^{-1} in the spectrum which are difficult to assign.

Saturated fatty acids have a slightly different spectrum (Figure 5.4). The spectra are all very similar which is not surprising as the structures only vary by the length of the carbon chain. The spectra exhibit bands in the ranges 2958 - 2955 cm^{-1}, 2930 - 2929 cm^{-1} and 2857 - 2856 cm^{-1} which are due to aliphatic C-H stretches and in the range 1470 - 1469 cm^{-1} which is indicative of aliphatic C-H deformations. The spectrum of stearic acid (VA21) contains an additional band at 2899 cm^{-1}. The band which is expected to occur near 1378 cm^{-1} is not evident, but a band appears in the range 1352 - 1351 cm^{-1}. A band is evident in the region 1413 - 1412 cm^{-1} which has been assigned to the C-H deformations in the methylene groups in the immediate vicinity of the carboxyl group. The spectra are also characterized by a band of medium intensity in the range 727 - 725 cm^{-1} which is

representative of the rocking vibrations of long chain aliphatic compounds.

The spectra of myristic (VA19) and palmitic (VA20) acid exhibit weak bands at 1599 cm^{-1} and all three fatty acid spectra contain an absorption in the range 1435 - 1433 cm^{-1} and one in the area 691 - 689 cm^{-1} which are regions which have been discussed earlier as being related to structures containing C=C bonds. These bands may result from impurities in the standard material. (They were obtained from Aldrich and were general purpose reagent quality). The spectrum may also be affected by polymorphism. It has been found that fatty acids may exist in more than one crystal structure. Two orientations of the hydrocarbon chain have been found with respect to the axes of the crystal and the hydrogen bonding within the molecule has been found to be different for the two forms. A spectrum of a mixture of alpha and beta forms of stearic acid was found to vary considerably from a spectrum of the beta polymorph only (Sinclair et al., 1952a). The spectrum of the mixture contains an absorption with maximum intensity centred at approximately 875 cm^{-1} which shifts to approximately 930 cm^{-1}. Unfortunately, the region between 1430 and 1500 cm^{-1} is not clearly presented in the figures

published in the literature and the region between 1320 and 1400 cm^{-1} is blocked by the absorptions due to the carbon disulphide solvent. Thus, it is not possible to see what effect polymorphism has in this region.

The spectra exhibit bands due to the carboxyl group. A very broad, weak shoulder is observed in all three spectra which commences near 3000 cm^{-1} and ends near 3400 cm^{-1} in the spectrum of myristic acid. The band goes off scale in the other two spectra. The spectra also contain a band in the region of 2669 - 2661 cm^{-1} which is characteristic of carboxylic acids. The carbonyl absorption falls in the range 1714 - 1711 cm^{-1} which corresponds with the value for fatty acids and a broad band occurs in the region 948 - 945 cm^{-1}. The width of the band may be due to the polymorphism. There is also a series of bands which occur in the following regions: near 1329 cm^{-1} (which occurs as a shoulder near 1330 cm^{-1} in the spectra of palmitic (VA20) and stearic (VA21) acids), 1312 - 1301 cm^{-1}, 1275 - 1262 cm^{-1}, 1251 - 1237 cm^{-1}, 1229 - 1213 cm^{-1}, 1208 - 1204 cm^{-1} (except for myristic acid) and 1192 - 1188 cm^{-1}. These bands are most probably related to the band progression which has been described for fatty acids and attributed to the wagging and

twisting motions of the methylene groups (Jones et al., 1952). The broad multiplet in the region of 1310 cm^{-1} is probably due to the coupled absorptions of the band progression and the C-O stretching vibrations (Jones et al., 1952). The number of bands in the progression is thought to be related to the length of the carbon chain, but this is often obscured by the C-O stretching mode in the carboxylic acid group (Jones et al., 1952). The bands are reported to be fairly evenly spaced (Jones et al., 1952), but the variations observed in these spectra may be due to the presence of more than one crystal form.

The spectra of the saturated fatty acids display sharp, fairly weak bands in the regions 1126 - 1125 cm^{-1}, 1104 - 1094 cm^{-1}, 817 - 812 cm^{-1}, 786 - 782 cm^{-1} and 552 - 551 cm^{-1}. In addition, the spectrum of palmitic acid (VA20) exhibits a band at 852 cm^{-1} and the spectra of myristic (VA19) and stearic (VA21) acids contain bands at 755 and 762 cm^{-1} respectively. The three spectra also show extremely weak bands in the region 1787 - 1785 cm^{-1} which appear as shoulders on the strong carbonyl absorption. These bands do not correspond to absorptions which are characteristic for fatty acid structures and consequently are difficult to

assign. They may result from impurities or the effects of polymorphism.

Identification of unknown samples

A survey was made of the surviving contents of a variety of ceramic and stone jars from the Egyptian collections of the British Museum and the Petrie collection (University College, London). The resulting spectra were grouped by similarities in the spectra and there were several groups which were thought to be mixtures. One of the groups showed similarities to the spectra of the saturated fatty acid spectra obtained by diffuse reflectance. The similarities are in the frequency values. The shape of the sample spectra are somewhat different. The variations may be due in part to the various degrees of degradation of the samples and possibly to the original material being a mixture. Also, other materials may have been added: many of the samples contained some chaff-like material and other contaminants. Because of the time constraints and the large number of samples, the specimens were not pretreated in any way. The ranges of frequency values are listed in Table 5.4 compared with those of the fatty acids and the oils. The sample details are listed at the end of the chapter.

The spectra contain absorptions due to C-H stretching and deformation vibrations in the regions 2943 - 2922 cm^{-1}, 2861 - 2852 cm^{-1} and 1474 - 1464 cm^{-1}. The spectra also exhibit a band in the region 1435 - 1420 cm^{-1} which was tentatively assigned to the methylene group stretches which were adjacent to the C=C. However, this absorption is also present in the saturated fatty acid spectra. The absorption which is expected near 1412 cm^{-1} is only present in one sample spectrum (MS15P) at 1413 cm^{-1} and as a weak shoulder in a few of the other sample spectra. The band which is expected in the region 1380 - 1370 cm^{-1} does not occur in the saturated fatty acid spectra, but is apparent in that of the unsaturated oleic acid. In the unknown sample spectra, it is apparent in only a few cases. The band which is present near 1352 cm^{-1} in the saturated fatty acid spectra appears in only a few of the sample spectra. The sample spectra all contain an absorption in the region 729 - 720 cm^{-1} which results from the aliphatic chain rocking vibration.

The spectra were subdivided into two groups based on the shape of the O-H stretching absorption. In the first group, which contains samples MS11, MS12, MS33, MS14, MS14P, MS18P and MS15P (Figure 5.4c), the O-H band appears as a broad band which begins

in the region of 3700 cm^{-1} and runs into the C-H absorptions at 3000 cm^{-1}. It is thought that part of this absorption may be due to moisture in the sample, but the same range appears for this absorption in the spectrum of myristic acid. The second group, which consists of samples MS38, MS2 (Figure 5.4b), MS30, MS10, MS5P, MS25, MS1 and MS26, exhibits a rounded absorption with maximum intensity which falls in the range 3495 - 3127 cm^{-1}. The band seems to run into the C-H bands. All of the spectra contain bands which correspond to those in the fatty acid spectra. There is, however, some variation and some evidence of ester content in a few of the sample spectra.

The group I samples all display the shoulder in the region between 3700 - 3000 cm^{-1} which was described above (Figure 5.4). The spectra also contain an absorption in the region 2683 - 2659 cm^{-1} which is characteristic of carboxylic acids. The spectra also contain the absorption centred near 945 cm^{-1} which is due to the O-H deformation in the carboxylic acid functional group. The evidence for a mixture of ester and carboxylic acid materials is seen in the carbonyl stretching region. In the spectra of samples MS11, MS14P, MS18P and MS15P, a band is observed in the region 1718 - 1714 cm^{-1} with a very weak shoulder on the higher

frequency side of the band. This is representative of the C=O stretch in the carboxylic acid group and the shoulder falls into the region which is characteristic for ester carbonyl stretches. The other samples, MS12, MS33 and MS14, exhibit bands with maximum intensity in the region of 1743 - 1742 cm^{-1} with weaker bands or shoulders (in the spectra of MS12, the bands are of equal intensity) in the region 1721 - 1719 cm^{-1} which indicate the presence of both types of carbonyl groups, esters and carboxylic acids. The region between 1330 - 1180 cm^{-1} shows some variation in the sample spectra. A characteristic band progression appears in the spectra of carboxylic acids in this region as does the C-O stretch in ester groups. In the spectra of group I which contain the maximum carbonyl absorption near 1717 cm^{-1}, bands occur in the regions 1314 - 1296 cm^{-1} and 1205 - 1189 cm^{-1} with three to four very weak bands in between these absorptions. In the spectra of MS12 and MS33 which contain the strong ester absorption, a broad shoulder appears from approximately 1314 cm^{-1} to 1195 cm^{-1} and from near 1318 cm^{-1} to 1188 cm^{-1} respectively. In the spectrum of MS14, a very indistinct absorption occurs in this region with maximum intensities at 1252 and 1190 cm^{-1}. It is interesting that the

spectra which seem to contain a greater amount of carboxylic acid, MS11, MS14P, MS18P and MS15P, exhibit indications of the fatty acid band progression and that in the spectra of the materials which seem to contain ester groups, the corresponding region is blurred. This may be due to the interference of the C-O absorptions which have been observed in triglyceride esters. Also, the complexity of the mixtures probably causes the general loss of resolution in this area.

The group I spectra are also characterized by fairly consistent absorptions in the regions of 813 - 811 cm^{-1}, 784 - 782 cm^{-1}, 693 - 687 cm^{-1} and 565 - 547 cm^{-1} with a weak shoulder in the region of 880 cm^{-1}. The bands were not assigned except for the band near 690 cm^{-1} which was assigned to the cis-isomer structure in unsaturated fatty acids, although it is also apparent in the saturated fatty acid spectra. Bands occur in the other regions in the spectra of the saturated fatty acids.

The group II spectra (Figure 5.4) contain some evidence for the presence of carboxylic acids, but it is less strong in most of the sample spectra. For example, only two spectra, MS5P and MS25, contain a carbonyl absorption with maximum intensity at

1703 and 1712 cm^{-1} respectively with weak shoulders in the higher frequency region. In the other sample spectra (MS38, MS2, MS30, MS10, MS1 and MS26), the maximum intensities in the carbonyl region fall between 1749 and 1736 cm^{-1} with a less intense band or shoulder in the area of 1717 - 1716 cm^{-1}. The spectra contain a shoulder in the area of 2685 - 2668 cm^{-1} which is, for many of the samples, less well defined than in the group I spectra. The spectra in group II also contain an absorption in the region of 957 - 938 cm^{-1} which is less distinct in some of the some spectra.

In the region of the band progression, 1350 - 1180 cm^{-1}, there is much variation. The spectra of samples MS1 and MS26 contain multiple bands with a band of maximum intensity at 1184 and 1185 cm^{-1} respectively. The spectra of MS25 and MS1 exhibit absorptions near 1319 - 1299 cm^{-1} and near 1195 cm^{-1} with several very weak bands in between. In the remaining four sample spectra, the region is less distinct with a shoulder which commences near 1327 - 1318 cm^{-1} and ends with the absorption in the range 1203 - 1184 cm^{-1}. In the spectrum of MS30, the region is fairly indistinct.

The group II spectra also exhibit absorptions near 812 - 804 cm^{-1}, 784 - 780 cm^{-1}, 690 - 657 cm^{-1} and near 557 - 552 cm^{-1} with a weak shoulder or band in the region of 893 - 850 cm^{-1}. However, there is a greater variation in the occurence of these bands.

The presence of bands in some of the spectra from both groups in the regions 1652 - 1621 cm^{-1} and 1598 - 1582 cm^{-1} may be indicative of the C=C stretches in unsaturated materials. However, with the absorption near 1502 - 1500 cm^{-1}, they may represent the presence of aromatic compounds as components of the mixture.

A possible explanation is that the samples are partially degraded triglycerides which would explain the presence of characteristic absorptions of both ester and fatty acid groups. The complexity of these samples causes variations in the spectra and makes it difficult to identify them with certainty. However, the appearance of certain characteristic bands of both fatty acids and esters in all of the spectra indicates the identity of the major components of the sample. The presence of fatty acids and esters suggests that the original material contained oils or fats

of some kind. However, it is not possible to identify the oil or oils and the identity of any minor constituents such as might occur in ungents cannot be determined. It would be necessary to use a sensitive separation technique such as gas chromatography to further elucidate the identity of the samples.

The conclusions reached from these samples may be compared with a report of the analysis of the contents of two glass bottles (Barag, 1972; Basch, 1972). In this study, the surviving contents of two glass vessels of uncertain provenance which were reported to have been found in the northern region of Jerusalem were analysed. The objects were thought to have been obtained from a tomb site. The contents which were thought to be original have survived (Barag, 1972). The contents consisted of a liquid residue with a covering which was described as a "dark brownish-red resinous material" (Basch, 1972). Samples were obtained of both and were analysed by infrared spectroscopy, thin layer chromatography and gas chromatography.

The infrared spectra were not shown, but the wavelengths of the major bands were reported. The liquid material, after the water and other volatiles were removed, gave spectra which exhibited a

broad band in the region of 3333 - 2500 cm^{-1} which was assigned to a bonded O-H vibration and a strong absorption at 1709 cm^{-1}. The conclusion was reached that the material contained a carboxylic acid functional group. Absorptions were also reported to have occurred at 1111 and 1031 cm^{-1} which were said to be indicative of glycerine. The conclusion was reached that fatty acids and glycerine in an aqueous solution were the major constituents of the liquid as there were no bands in the spectra which resulted from functional groups which do not occur in fatty acids and glycerol (Basch, 1972).

The infrared spectra of the brownish-red samples were similar to each other and were reported to exhibit bands which were characteristic of both organic acids and esters (Basch, 1972). Bands were observed in the regions of 2941, 2857, 1460, 1379 and 722 cm^{-1} which were reported to be characteristic of "a long linear aliphatic chain," (Basch, 1972) although only the band at 722 cm^{-1} is specifically due to long aliphatic chains. Also, a flattened, broad O-H band was found in the region 3571 - 2500 cm-1 in addition to a strong band at 1709 cm^{-1}. The absorptions are characteristic of a carboxylic acid. The description of the carbonyl absorption is interesting as a shoulder is reported to

occur at 1733 cm^{-1} which was assigned as an ester absorption. This spectral feature is very similar to those found for the jar contents examined in this study. The spectra also contained bands in the region 1250 - 1111 cm^{-1} which were assigned to ester C-O vibrations and were described as "diffuse absorptions" (Basch, 1972). This pattern may also correspond to the same region in the spectra obtained for this thesis where a variety of absorption patterns were observed. The conclusion reached by Basch based on the infared results was that the materials were probably a fat or oil which had undergone a large degree of hydrolysis.

In the study (Basch, 1972), thin layer chromatography was used to analyse the "resins" and the samples were found to contain mono- and di-glycerides as well as fatty acids. Triglycerides were not observed. The gas chromatography results suggested olive oil as a possible original material due to the high ratio of palmitic acid to stearic acid which was found and the high amount of oleic acid which has survived. Oleic acid would be expected to alter over time due to the reactivity of the double bond (Basch, 1972).

One of the jar samples in this thesis, MS18P, was analysed by gas

chromatography/mass spectrometry (White, personal communication). The material was examined before and after saponification and it was found that almost all of the fatty acid material exists as free fats. No triterpenoid or diterpenoids were isolated which indicates that no resinous compound is present (Chapter 7). The principal components were found to be palmitate and stearate which result from palmitic and stearic acid. Evidence was found of the C-8, C-9 and C-10 dicarboxylic acids which indicate that the original material contained semi-drying, unsaturated oils. This suggests either a fruit or seed oil as vegetable oils are higher in polyunsaturated fats. Some animal fat may have been present. No sterols or cholesterol were isolated. However, such materials are susceptible to bacteria action and would have degraded if the sterols had been present originally. No ketone or aldehyde functional groups were present in the sample. The conclusion was reached that the original material was probably a seed or fruit oil with the possible addition of animal fat (White, personal communication).

Unknown sample information

Group I

MS11 Medium brown, gummy residue from one handled, alabaster (?) jug with peg base. Provenance - unknown. Date - New Kingdom (XVIIIth dynasty). British Museum Department of Egyptology 26962.

MS12 Dark brown, waxy residue from one handled, sepentine vase with lid. Provenance - unknown. Date - New Kindom (XVIIIth dynasty). British Museum Department of Egyptology 24417.

MS14 Orange waxy residue from one handled alabaster (?) jug with lid. Provenance - unknown. Date - (New Kingdom) XVIIIth dynasty. British Museum Department of Egyptology 24418.

MS33 Buff pink, soft residue from imitation (?) alabaster (?) barrel jar on stand with lid. Provenance - unknown. Date - New Kingdom (?). British Museum Department of Egyptology 69024.

MS14P Brown, sticky residue from thin wavy handled pottery cylinder jar. Provenance - Hu. Date - Predynastic. British Museum Department of Egyptology 30902.

MS15P As above, lighter brown, loose residue which had been

removed from jar previously and stored in polythene bag.

MS18P Black, shiny, friable residue from "Abydos ware" pottery jar. Provenance - Abydos, tomb of Djer. Date - Protodynastic (Ist dynasty). British Museum Department of Egyptology 35549.

Group II

MS1 Yellow-brown, sticky residue from alabaster (?) globular vase with flattened base. Provenance - Reqoquah ?? tomb 1. Date - New Kingdom, (XVIIIth dynasty). University College London Petrie Collection 38053.

MS2 Orange-brown, compact residue from large alabaster (?) jar with two loop handles on body. Provenance - unknown. Date - New Kingdom (XVIII - XIX th dynasty). University College London Petrie Collection 38052.

MS10 Medium brown residue from blue anhydrite cylinder jar. Provenance - unknown. Date - Middle Kingdom (XIIth dynasty). British Museum Department of Egyptology 4490.

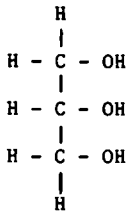
MS25 Light brown, powdery residue from rounded anhydrite jar with moulded rim. Provenance - unknown. Date - Middle Kingdom (XIIth dynasty). British Museum Department of Egyptology 4705.

MS26 Pale yellow, waxy residue which appears black on the surface from an alabaster (?) wide neck globular vase on base. Provenance - unknown. Date - ?New Kingdom. British Museum Department of Egyptology 32067.

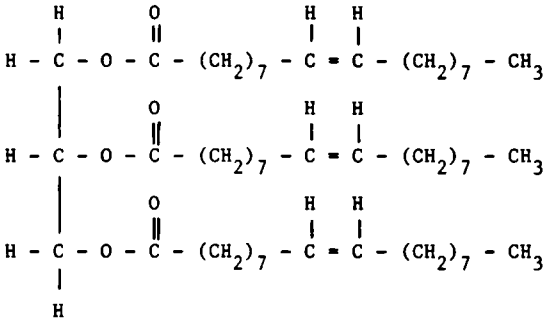
MS30 Orange, friable residue which appears black on the surface from a round, alabaster (?) jar. Provenance - unknown. Date - Late Old Kingdom to Early Middle Kingdom (?)(VI - XIth dynasty). British Museum Department of Egyptology 35319.

MS38 Reddish-brown, soft residue from alabaster (?), one handled toilet jar with a wide neck. Provenance - Thebes, toilet box of Tutu. Date - New Kingdom (XVIIIth dynasty). British Museum Department of Egyptology 24708 (number for entire box and contents).

MS5P Black/brown fibrous residue from one handled pottery jug with loop handle on body. Provenance - unknown. Date - New Kingdom (XIX - XXIIth dynasty). British Museum Department of Egyptology 4902.



(a)



(b)

Figure 5.1 Structure of (a) glycerol and (b) triolein, a simple triglyceride.

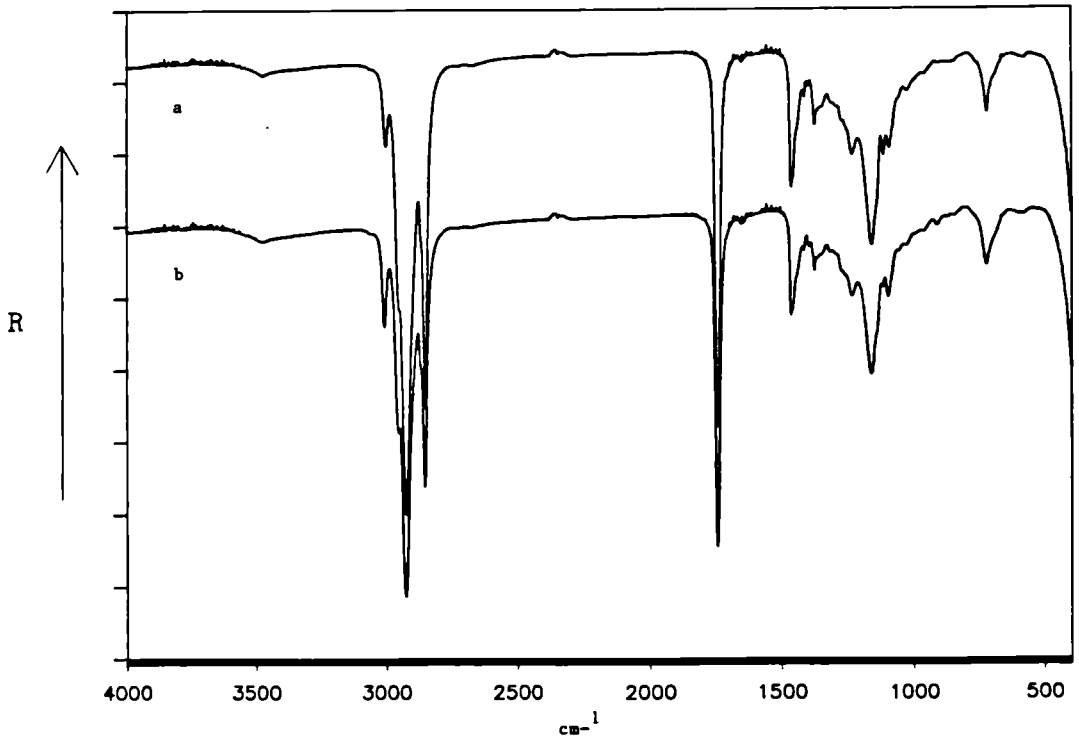


Figure 5.2 Transmission spectra of (a) olive oil (GS9 Commericial source) (gsva0465) and (b) grapeseed oil (GS11 Commercial source) (gsva0467)

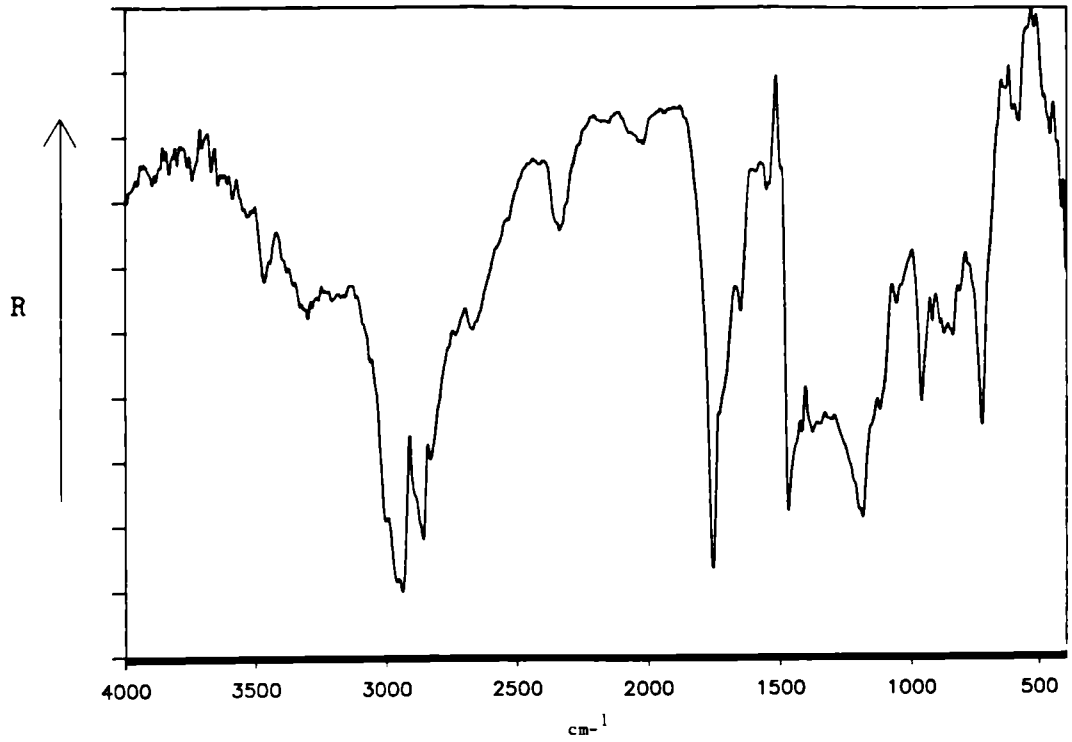


Figure 5.3 Diffuse reflectance FT-IR spectrum of lamb's suet (GS8) (gsva0434).

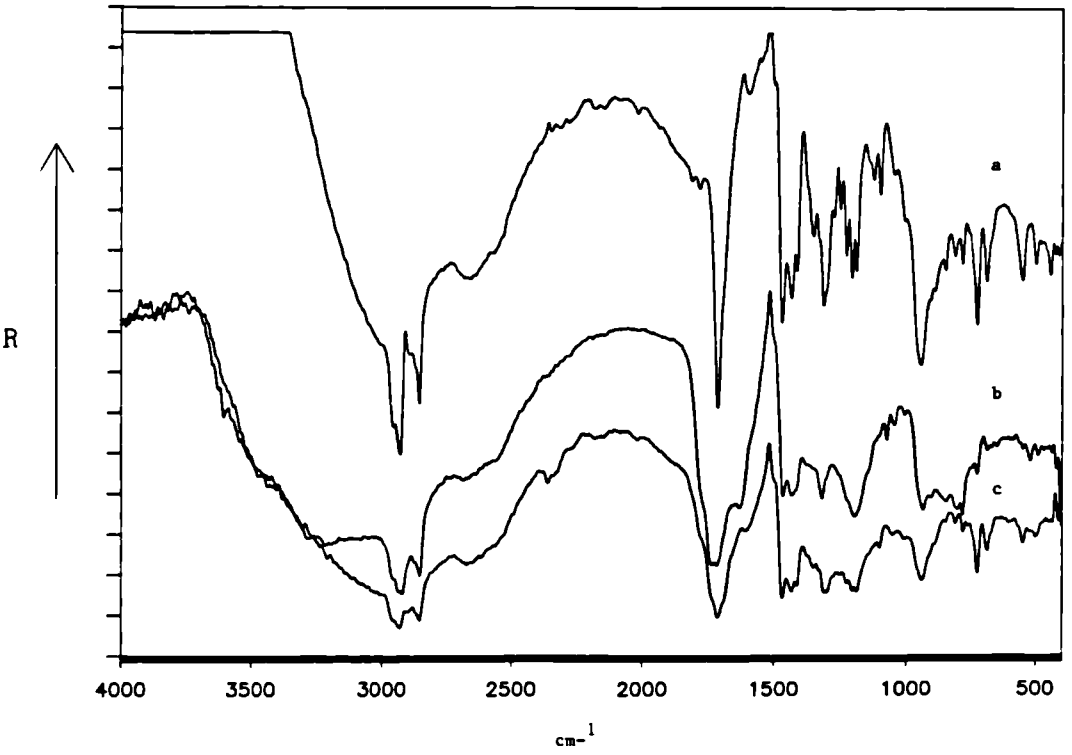


Figure 5.4 Diffuse reflectance FT-IR spectra of (a) palmitic acid (VA20 BDH Chemicals Ltd.) (gsva0473), (b) residue from Egyptian calcite jar - Group II (MS2 UC38052) (gsva0409) and (c) residue from Egyptian ceramic jug - Group I (MS15P BM30902) (gsva0458).

TABLE 5.1

Major fatty acids of oils and fats (Mills and White, 1987)

Formula	Systematic name	Common name	Structure	M.p. °C
$C_{12}H_{24}O_2$	Dodecanoic	Lauric	$HOOC-(CH_2)_{10}-CH_3$	44
$C_{14}H_{28}O_2$	Tetradecanoic	Myristic	$HOOC-(CH_2)_{12}-CH_3$	54
$C_{16}H_{32}O_2$	Hexadecanoic	Palmitic	$HOOC-(CH_2)_{14}-CH_3$	63
$C_{16}H_{30}O_2$	9-Hexadecenoic	Palmitoleic	$HOOC-(CH_2)_7-CH=CH-(CH_2)_5-CH_3$	0.5
$C_{18}H_{36}O_2$	Octadecanoic	Stearic	$HOOC-(CH_2)_{16}-CH_3$	70
$C_{18}H_{34}O_2$	9-Octadecenoic	Oleic	$HOOC-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$	16
$C_{18}H_{32}O_2$	9,12-Octadecadienoic	Linoleic	$HOOC-(CH_2)_7-CH=CH-CH_2\,CH=CH-(CH_2)_4-CH_3$	-5
$C_{18}H_{30}O_2$	9,12,15-Octadeca-trienoic	Linolenic	$HOOC-(CH_2)_7-CH=CH-CH_2\,CH=CH-CH_2-CH=CH-CH_2-CH_3$	-11
$C_{18}H_{30}O_2$	cis,trans,trans-9,11, 13-Octadecatrienoic	α-Elaeostearic	$HOOC-(CH_2)_7-CH=CH-CH=CH-CH=CH-(CH_2)_3-CH_3$	49
$C_{18}H_{34}O_2$	12-Hydroxy-9-octa-decenoic	Ricinoleic	$HOOC-(CH_2)_7-CH=CH-CH_2-CHOH-(CH_2)_5-CH_3$	

TABLE 5.2

Fatty acid composition of some oils and fats (Mills and White, 1987)

	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	Others
Olive				tr	8-18	2-5	56-82	4-19	0.3-1	
Sunflower seed				tr	5-6	4-6	17-51	38-74	tr	
Coconut	5-9	6-10	44-52	13-19	8-11	1-3	5-8	1-2		
Poppyseed					10	2	11	72	5	
Walnut					3-7	0.5-3	9-30	57-76	2-16	
Linseed				tr	6-7	3-6	14-24	14-19	48-60	
Hempseed					6-7	2-3	12-17	55-65	14-20	
Perilla					7	2	13	14	64	
Tung					3	2	11	15	3	elaeostearic 59%
Castor					1-2	1-2	3-6	4-7		ricinoleic 83-89%
Pig				1-2	20-28	13-16	42-45	8-10	0.5-2	
Beef tallow				2-3	23-30	14-29	40-50	1-3	0-1	
Mutton tallow				6	26	30	30	1.5	0.2	
Cow's milk	1-2.5	2-3	2-3	9-11	22-30	11-15	25-31	1-2.5	1-2.5	
Hens eggs				tr	27	9	44	13.5	0.5	

The headings, 18:0, 18:1, etc. indicate chain lengths:number of double bonds. These data were all obtained by gas chromatography, and are from several sources notably T. P. Hilditch and P. N. Williams, The Chemical Constitution of Natural Fats and D. Swern (editor), Bailey's Industrial Oil and Fat Products. For several oils there are few reliable data and it is not possible to give a range of compositions.

TABLE 5.3

Frequency values and band assignments for vegetable oils and lamb suet

Vegetable oils cm-1	Lamb suet GS8 cm-1	Vibration	Functional group	Frequency values given in literature cm-1	Ref.
3477 - 3472(w)	3468(w)	O-H stretch	water		
	3304(w)	O-H stretch	carboxylic acid	3000 - 2500(b)	4
				3333 - 3030	3
				3500 - 3000	1
3009 - 3005(m)	3010(w)	C-H stretch	C=C bond	3100 - 3000(va) (3020)	2
				3030(s)	3
2954(sh)	2940(s)	C-H stretch	methyl group	2960(m)	1
2926 - 2925(s)		C-H stretch	methylene group	2920(s)	1
2855 - 2854(s)	2862(s)	C-H stretch	methylene group	2850(s)	1
	2835(m)	C-H stretch	methylene group	2850(s)	1
	2671(w)	O-H stretch	carboxylic acid	near 2650(w)	4
				2703	3
1747 - 1746(s)	1756(s)	C=O stretch	ester (triglyceride)	1751 - 1748	3
	1735 - 1680(sh)	C=O stretch	carboxylic acid (fatty acid)	1701 - 1698	1
				1715 - 1709	3
1657 - 1656(vw)	1654(w)	C=C stretch	C=C bond	1650 - 1580(sh)	2
* 1650(vw)		C=C stretch	C=C bond	1650 - 1580(sh)	2
1466(m)	1471(s)	C-H asym. deformation	methyl group	1450 ± 20(m)	4
		C-H deformation	methylene group	1465 ± 20(m)	4
near 1430(sh)	near 1440(sh)	C-H deformation	methylene group next to C=C bond	1435	2
near 1417(vw)	1418(w)	C-H deformation	methylene group next to carboxylic acid	1410 - 1405	1,2
1378(w)	1379(w)	C-H deformation	methyl group	1389 - 1351	3

TABLE 5.3 contd.

Frequency values and band assignments for vegetable oils and lamb suet

Vegetable oils cm-1	Lamb suet GS8 cm-1	Vibration	Functional group	Frequency values given in literature cm-1	Ref.
	1300 - 1200(sh)	C-H 'wagging and twisting' vibration	methylene groups in fatty acids	1350 - 1180 band progression series of weak evenly spaced bands	5
1239 - 1238(w)		C-O stretch	ester (triglyceride)	near 1250	3
1164 - 1163(m)	1184(s)	C-O stretch	ester (triglyceride)	near 1163	3
** 1120 - 1119(w)	1121(w)	C-O stretch	ester (triglyceride)	1121	3
1100 - 1097(w)		C-O stretch	ester (triglyceride)	1101 - 1099	3
	1060(w)	unassigned			
near 970(vw)	964(m)	C-H out-of-plane deformation	C=C bond (trans-)	980 - 965(s)	2
	922(m)	unassigned			
	840(w)	unassigned			
724 - 723(m)	727(m)	chain rocking vibration	long chain hydro-carbons with four or more methylene units	750 - 720(m)	4
				719	3
					1,2
near 670(sh)	near 690(vw sh)	C-H out-of-plane deformation	C=C bond (cis-)	near 690	2

* Absorption is not apparent is some spectra.

** Absorption occurs in spectra of samples GS10, GS11 and GS12.

1. Sinclair et al., 1952a
2. Sinclair et al., 1952b
3. Shreve et al., 1950
4. Bellamy, 1975
5. Jones et al., 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 5.4

Frequency values and band assignments for fatty acids and samples from Egyptian jars

Fatty acids VA18 cm-1	VA19 cm-1	VA20 cm-1	VA21 cm-1	Unknown jar contents cm-1	Vibration	Functional group	Frequency value given in literature cm-1	Ref.
********** (see text) **********				see text	O-H stretch	carboxylic acid	3000 - 2500(b)	4
						hydrogen bonded	3333 - 3030	3
							3500 - 3000	1
3006(m)					C-H stretch	C=C bond	3100 - 3000(va) (3020)	2
						C=C bond	3030(s)	3
	2958(s)	near 2955(sh)	2955(s)		C-H stretch	methyl group	2960(m)	1
2925(s)	2929(s)	2930(s)	2930(s)	2943 - 2922(s)	C-H stretch	methylene group	2920(s)	1
			2899(m)		C-H stretch	methine group	2890 ± 10(w)	4
2854(s)	2856(s)	2857(s)	2856(s)	2861 - 2852(s)	C-H stretch	methylene group	2850(s)	1
2675(w)	2669(w)	2661(w)	2668(w)	* 2685 - 2659(w)	O-H stretch	carboxylic acid hydrogen bonded	near 2650(w)	4
	1786(sh)	1785(sh)	1787(sh)		unassigned			
				* 1749 - 1736(s)	C=O stretch	ester (triglyceride)	1751 - 1748	3
1711(s)	1713(s)	1714(s)	1711(s)	* 1721 - 1703(s)	C=O stretch	carboxylic acid (fatty acid)	1701 - 1698	1
							1715 - 1709	3
				* 1652 - 1621(w)	C=C stretch	C=C bond	1650 - 1580(sh)	2
	1599(w)	1599(w)		* 1598 - 1582(w)	C=C stretch	C=C bond	1650 - 1580(sh)	2
				* 1502 - 1500(w)				
1466(m)	1470(m)	1470(m)	1469(m)	1474 - 1464(s)	C-H asym. deformation	methyl group	1450 ± 20(m)	4
					C-H deformation	methylene group	1465 ± 20(m)	4
1434(m)	1435(m)	1434(m)	1433(m)	1435 - 1420(va)	C-H deformation	methylene group next to C=C bond	1435	2
1413(m)	1412(m)	1413(m)	1412(m)	* 1413(va)	C-H deformation	methylene group next to carboxylic acid	1410 - 1405	1,2
1378(w)				* 1391 - 1376(va)	C-H deformation	methyl group	1389 - 1351	3

TABLE 5.4 contd.

Frequency values and band assignments for fatty acids and samples from Egyptian jars

Fatty acids				Unknown jar	Vibration	Functional group	Frequency value given	Ref.
VA18	VA19	VA20	VA21	contents			in literature	
cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
	1352(m)	1351(w)	1352(m)	* 1352(va)	C-H 'wagging and	methylene groups in	1350 - 1180	5
	1329(w)	near 1330(sh)	near 1330(sh)	1337 - 1296(va)	twisting' vibration	fatty acids	band progression	
	1310(m)	1312(m)	1301(m)				series of weak	
1285(m)	1263(m)	1275(w)	1262(m)	see text			evenly spaced bands	
1247(m)	1237(m)	1251(w)	1241(m)					
	1213(m)	1229(m)	1223(m)					
		1208(m)	1204(m)	* 1205 - 1184(s)	C-O stretch	ester (triglyceride)	near 1163	3
	1192(m)	1190(m)	1188(m)					
				1140(va)	unassigned			
1119(w)	1126(w)	1125(w)	1125(w)	1116 - 1102(va)	unassigned			
1091(w)	1094(w)	1100(w)	1104(w)		unassigned			
939(m)	945(m)	948(s)	947(s)	* 957 - 938(va)	O-H deformation	carboxylic acid	near 935	3
		852(w)			unassigned			
	817(m)	814(w)	812(m)	* 813 - 804(va)	unassigned			
	782(w)	784(w)	786(w)	784 - 780(va)	unassigned			
	755(m)		762(m)		unassigned			
723(m)	725(m)	727(m)	726(m)	729 - 720(m)	chain rocking	long chain hydro-	750 - 720(m)	4
					vibration	carbons with four or	719	3
						more methylene units		
	689(m)	691(m)	690(m)	* 693 - 675(va)	C-H out-of-plane	C=C bond (cis-)	near 690	2
					deformation			
	552(m)	552(m)	551(m)	* 565 - 547(va)	unassigned			
	506 - 501(m)				unassigned			

* Absorption is weak or not apparent in some spectra.

1. Sinclair et al., 1952a
2. Sinclair et al., 1952b
3. Shreve et al., 1950
4. Bellamy, 1975
5. Jones et al., 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

CHAPTER 6 BITUMINOUS MATERIALS

Bitumen

Source

Bitumen has been defined (Abraham, 1938) as "a generic term applied to native substances of variable colour, hardness and volatility; composed principally of saturated hydrocarbons substantially free from oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being fusible and largely soluble in carbon disulphide."

Bituminous materials are fractions of petroleum which is fossilized organic material. The materials are produced over a very long period of geological time from biological remains which were deposited in layers. Chemical and biological reactions alter the structure of the organisms. The composition of the lower sections were subsequently affected by the anaerobic conditions, increased temperature and pressure. The reactions involved the eventual loss of functional groups and molecules were broken up. Other alterations included the loss of side chains and the transfer of hydrogen atoms from one molecule to another which produced saturated and unsaturated materials. Functional groups may still exist in more recent layers which

have been exposed to relatively mild environments (Mills and White, 1987). Thus, the composition of bitumens is related to that of the original organisms (Mills and White, 1987).

The classification and nomenclature is not clear for these materials. Writers in antiquity used many terms and often only distinguished between liquid, solid or semi-solid. Also, modern nomenclature has not been consistent (Forbes, 1936). The term asphalt is the Greek name and bitumen is the Roman word for the same substance (Mills and White, 1987). The material may be considered in four groups, the bitumens, pyrobitumens, the pyrogeneous distillates and the pyrogeneous residues. The bitumen group includes petroleums, native asphalts and bitumens and the asphaltites which include gilsonite and glance pitch. The pyrobitumens include peat, lignite and coal (Forbes, 1936). The third and fourth groups are artificial materials made by pyrolysis of wood, coal or resin. The distillate produced by the pyrolysis is known as tar and the residue is referred to as pitch (Forbes, 1936; Mills and White, 1987). The term bitumen is now used for the material which is composed of a large quantity of hydrocarbon components known as maltenes which are soluble in organic solvents and a low percentage of insoluble constituents

known as asphaltenes. Bitumens contain little or no inorganic material (Mills and White, 1987), and the term is utilized to describe both the substances which occur naturally and the involatile substance left by petroleum distillation. In contrast, asphalts are considered to be the native deposits which occur as outcrops. They are classified by mineral content: true asphalts which contain less than 10% inorganic matter and rock asphalts which contain mineral matter in quantities greater than 10% (Forbes, 1936; Mills and White, 1987). Asphaltites are materials with a higher melting point and are sometimes infusible (Mills and White, 1987).

The ancient civilizations were not aware of the geological structure beneath the earth and obtained the bitumenous materials from surface deposits. The layers or strata beneath the earth's surface which contain petroleum hold natural gas and water in their pores along with the oil. The gas, which is a product of the decomposition of the materials which form the petroleum, results in high pressures which are held underground by impervious cap rock layers of clay or shale. If the cap rocks are disturbed by movements of the earth, fissures or gaps are created and the petroleum, gas and water can reach the surface to form

pools or seepages on the surface (Forbes, 1936). Layers nearer the surface may also be uncovered by erosion. The volatile portions evaporate over time leaving the heavy oil residue. (Mills and White, 1987) Also in some cases, oil strata do not stay underground and veins extrude to the surface. The natural gases escape and the volatile fractions evaporate slowly. The heavier fractions remain in the rock. Rock asphalt outcrops which contain 4 - 20% bitumen occur all over the world and were possible sources in antiquity. Veins of asphaltites and asphaltic pyrobitumen are much less common, but surface deposits may have been exploited in antiquity (Forbes, 1936).

Crude oil, asphalt, rock asphalt, petroleum asphalt, wood tar and wood tar pitch are the bitumenous materials which are believed to have been exploited in antiquity. Bitumen, wood tar and pitch were mixed with mineral matter to use as mortar, plaster and waterproofing material. The artificial mixture is referred to as mastic by archaeologists (Forbes, 1936) and care must be taken with the interpretation of the term. Certain forms of Pistacia resins are also referred to as mastic. There are a few classical records of bitumen collection and almost none on refinement techniques. It is assumed that heating was used to refine crude

asphalts and to prepare mastic. The major area of surface deposits in the Old World is in the fertile cresent, but other sources are found in Syria and in the Dead Sea. The material was used by the Assyrians for construction. Deposits have also been found in India and Eastern Europe (Forbes, 1936). As small deposits are located all over the world and may have been exploited on a small scale, identification of a bitumen is not strictly limited to objects from the Middle East.

Composition

The composition of bitumenous material is very complex and the fairly recent development of gas chromatography and subsequently, gas chromatography/mass spectroscopy has enabled workers to separate and identify the many hundreds of constituents (Mills and White, 1987). A detailed discussion of the many structures is beyond the scope of this thesis. However, the major families of compounds which are listed in the literature include normal, branched chain and cyclic hydrocarbons; diterpenoids; tetracyclic and pentacyclic triterpanes; and the acyclic isoprenoids, phytane and pristane. Examples of the principal groups, sterane (tetracyclic) and hopane (pentacyclic) skeleton structures are given in Figure 6.1. The diasteranes, which are structural

analogs of sterane in which there is a rearrangement of the configuration along the sterane backbone, have also been isolated. Bitumens may be characterized by the presence of hopanes of an analogous series of 17 beta (H),21 beta (H) hopanes. The diasteromers at positions R-22 and S-22 of the extended hopanes containing 31-35 carbon atoms have also been isolated. Monoaromatic analogs of steroid structures and polynuclear aromatic hydrocarbons have been cited. (Douglas and Grantham, 1974; Simoneit, 1977; Seifert and Moldowan, 1978; Simoneit and Lonsdale, 1982; Richardson and Miller, 1982; Venkatesan et al., 1982).

The compositions reported in the literature listed above vary widely quantitatively. They are affected by the depositional conditions, the age of the sample and the type of material which was deposited. For example, the presence of diterpenoids which have structures that are analogous to abietane and pimarane (constituents of higher plants) are thought to result from deposits of terrestrial material (Simoneit, 1977; Richardson and Miller, 1982). Geological deposits which contain large quantities of pentacyclic triterpenoids are thought to results from decay of marine material as the pentacyclic materials are

found in the structure of algae (Mills and White, 1987). The composition is also affected by the age of the deposit. Geologically older petroleums contain a higher amount of saturated material. Also, the concentration of tricyclic and pentacyclic triterpanes decreases with increasing age of the deposits (Seifert and Moldowan, 1978). The extent of biodegradation is also associated with the age of the deposit. For example, isoprenoid compounds degrade more swiftly than steranes and terpanes which have been observed to withstand moderate amounts of biological attack. However, steranes are completely degraded in very old crude petroleums. While the diasterane content also decreases, they survive to a certain extent (Seifert and Moldowan, 1979). The hopane compounds are thought to be a ubiquitous component of sediments as hopane structures have been isolated in every sediment analysed thus far (Ourisson et al., 1979; Ourisson et al., 1984). It is thought that the hopanes are incorporated in the cell membranes of the bacteria which instigate the decay of plant and animal matter. Thus, when the bacteria are buried, they die and form part of the fossil layers (Ourisson et al., 1984). In spite of the difficulties of degradation, it seems to be possible to identify

bituminous substances by isolating the biological markers which are analogues of the original deposited materials (Mills and White, 1987).

Identification and interpretation of standard spectra

The identification of bituminous materials from several archaeological specimens was made by isolation of hopane species utilizing gas chromatography/mass spectrometry (Mills and White, 1987). The complexity and variation in composition coupled with the lack of distinctive functional groups makes FT-IR an unlikely choice for the characterization of bituminous materials. Nevertheless, series of bitumens from various sources was obtained and the diffuse reflectance spectra of the samples were recorded. An added difficulty with this study is that although most of the samples were obtained from the British Museum (Natural History) and the Institute of Archaeology mineralogy collection, the materials were not adequately catalogued and there is no record of how the identity (ie bitumen or asphalt), was determined. Most of the samples used in the study did have some sort of geological provenance (see appendix). However, no clear pattern was established between those samples marked bitumen and those labelled as asphalt. The samples were

classified according to similarities in the spectra and not by the original designation. Three samples obtained from Raymond White (National Gallery) were known to be bitumen, asphaltum and asphaltite and these samples were utilized to classify the other samples. Seventeen samples were found to have similar spectra, but they were further classified as group I (seven samples) and group II (ten samples) based on slight differences in the spectra. The samples of asphaltum and asphaltite fell into group II. A third group of samples was marked by further differences. Two spectra were marked with strong bands which may be due to inorganic matter.

The majority of the bitumen/asphalt sample spectra from groups I (Figure 6.2a) and II (Figure 6.3a) are simple spectra which indicate the nature of the materials as hydrocarbon mixtures. The characteristic strong bands occur in the regions of 2933 - 2924 cm^{-1}, 2866 - 2855 cm^{-1}, 1464 - 1459 cm^{-1} and 1379 - 1376 cm^{-1} for group I and in the regions of 2929 - 2923 cm^{-1}, 2869 - 2855 cm^{-1}, 1461 - 1457 cm^{-1} and 1379 - 1377 cm^{-1} for those in group II. These absorptions are due to the C-H stretching and bending vibrations (see Table 6.1) These band regions are also characteristic for the paraffin waxes and may be differentiated

by the fact that the wax is a fairly simple chemical structure compared to the mixture in the asphalts. The presence of a melange of materials results in fairly broad bands which are generally less intense than the bands due to the C-H stretching modes. Both of the groups are also sometimes characterized by bands in the regions of 882 - 860 cm^{-1}, 820 - 813 cm^{-1} and 753 - 744 cm^{-1} for group I and 879 - 871 cm^{-1}, 821 - 800 cm^{-1} and 758 - 743 cm^{-1} for group II. These bands vary considerably in intensity between samples and all three absorptions are not always present in every sample spectrum. They are thought to be due to the C-H out-of-plane deformations arising from the aromatic ring and are characteristic of the substitution pattern (see Table 6.1).

Groups I and II are differentiated by the region between 1700 - 1600 cm^{-1} in the spectra. In the group I spectra, the region is characterized by the presence of a band in the region 1605 - 1598 cm^{-1} and a less intense band located in the region 1652 - 1647 cm^{-1} which is very weak in some of the sample spectra. The spectra in group II contain a band in the region of 1706 - 1695 cm^{-1} and one in the region of 1607 - 1598 cm^{-1}. Some of the spectra in the second group also exhibit a band in the area of

1660 - 1645 cm^{-1}. The relative intensities of the bands in this group are variable. The spectra in group I are characterized by an absence or only a very weak shoulder in the region of 1706 - 1695 cm^{-1}. The bands in the region of 1607 - 1598 cm^{-1} and 1605 - 1598 cm^{-1} may be the result of the skeletal ring breathing mode in aromatic compounds, although the other bands which are normally associated with it are not present. The other two bands are more difficult to assign. The band in the region of 1700 cm-1 occurs in a region which is normally characteristic of oxygenated functional groups, such as the carbonyl group. There are very few other possibilities for identification and the assignment of this absorption is not clear. Although the range is slightly high for the values given by Bellamy (1975) of 1625 - 1575 cm^{-1}, the band in the region of 1645 - 1660 cm^{-1} and 1652 - 1647 cm^{-1} may be one of the degenerate pair of aromatic skeletal ring breathing modes.

The very weak bands in the region between 1209 and 1143 cm^{-1} may be due to vibrations arising from branched chain alkanes which are reported to be uncharacteristic due to wide ranges of possible frequency and very weak intensity (Bellamy, 1975). However, these bands occur near regions which are characteristic

of isopropyl groups (1170 ± 5 cm^{-1}, 1170 - 1140 cm^{-1}) and of tertiarybutyl groups (1250 ± 5 cm^{-1}, 1250 - 1200 cm^{-1})(Bellamy, 1975). The two bands in the regions of 1049 - 1018 cm^{-1} and 958 cm^{-1} (group I) and in 1043 - 1014 cm^{-1} and 960 - 917 cm^{-1} (group II) fall into the ranges given by Bellamy (1975) for the pair of absorptions due to cyclohexane (1055 - 1000 cm^{-1} and 1005 - 925 cm^{-1}). There is only one spectrum which exhibits a band at 727 cm^{-1} in addition to the band in the region of 758 - 743 cm^{-1}. However, a shoulder often occurs on the band near 758 - 743 cm^{-1}. This indicates that there is not a high percentage of long straight chain hydrocarbons in the structure.

The third group includes three spectra which show some similarities, but are somewhat variable. This group contains the sample identified as bitumen from the National Gallery. All three of the spectra exhibit bands in the region of 2928 - 2925 cm^{-1} and near 2857 cm^{-1} which are characteristic of the C-H stretch vibration. The band which occurs within the range (1465 - 1446 cm^{-1}) is in agreement with the values given by Bellamy (1450 ± 20 cm^{-1} and 1465 ± 20 cm^{-1}) for C-H deformation vibrations. However, the band which is expected to occur in the region of 1380 - 1370 cm^{-1} is only evident in the first sample spectrum at

1382 cm^{-1}. The samples are characterized by a band which is centred in the region of 1617 - 1595 cm^{-1} and is probably the result of aromatic skeletal stretching mode. There is great variation in the spectra in the region 1250 - 700 cm^{-1} which is indicative of a variation in chemical composition. Also, the bands are observed to be broad which also suggests the presence of a mixture. The first sample, RW2 is also characterized by weak bands at 2516, 1796, 874 and 715 cm^{-1} which are characteristic of calcium carbonate (Miller and Wilkins, 1952).

Two of the samples which were labelled as bitumen and rock asphalt were found to exhibit strong bands in the regions 2530 - 2516 cm^{-1}, 1817 - 1797 cm^{-1}, 880 - 878 cm^{-1} and 730 - 715 cm^{-1} which are characteristic of calcium carbonate (Miller and Wilkins, 1952). In addition, the rock asphalt spectrum has a very broad band with maximum intensities of 1433 and 1400 cm^{-1} which correspond to a strong absorption at 1430 cm-1 recorded in the literature for calcium carbonate The spectra also have evidence of an organic component with two absorptions in the regions of 2926 - 2925 cm^{-1} and 2860 - 2855 cm^{-1}. The C-H deformation absorptions, however, seem to be masked by the strong absorption near 1430 cm^{-1}. Also, there are bands which occur in

the region of 1200 - 1020 cm^{-1} which may be due to organic materials. The presence of the inorganic matter interferes with the interpretation of the spectrum.

Identification of unknown samples

Although there is some difficulty in identifying bituminous materials using infrared, two samples were tentatively identified as bituminous by the simplicity of their spectra and comparison with spectra in groups I and II. The first sample (KA4) was of material which was purchased in a street market in Ankara, Turkey and thought to be refined asphalt. It was desirable to confirm the identification as the material was to be used for experimental tool making. A spectrum was obtained and the values of the frequencies are listed in Table 6.1. The spectrum (Figure 6.2b) was found to resemble those in group I most closely. The sample spectrum exhibited bands at 2947, 2920, 1600, 1465, 1378, 865, 812 and 750 cm^{-1} which correspond to those observed for the group I materials. Also, there are weak absorptions in the area of 2850, 1210, 1030 and 725 cm^{-1} which support the possible identification of the sample as a bituminous substance.

The second sample was a black residue (KA1) which was parallel to the unpolished edge of a flint sickle blade from the Institute of Archaeology Mallowan collection from the site Arpachiyah dating from the Halaf period (possible 5th mellenium) . The blade is truncated at one end and broken at the other. The edge exhibits a gloss and is retouched with slight irregular denticulation. The location of the black deposit indicated that it might have been utilized as hafting material. A small sample was removed with the silicon carbide paper and the spectrum was obtained. The spectrum (Figure 6.3b) was fairly simple and is similar to those of the bituminous material in group II. The spectrum is characterized by absorptions at 2928, 2855, 1702, 1460, 1379, 1119, 1033 and 754 cm^{-1}. Also, there is a band in the region of 1600 cm^{-1} and there are several very weak bands in the region of 900 - 800 cm^{-1} which further support the identification.

Shale, jet and dopplerite

Source

Shale and jet are bituminous materials which have been used since antiquity for decorative objects. Jet has been defined as "essentially a very hard coal" (Mills and White, 1987). Shale is sedimentary rock composed of clay minerals and quartz, calcite,

pyrite and (carbonaceous) organic substances. However, the composition is variable, the clay content ranges from nearly 100% to 40% and the other constituents are not constant. Although these materials are formed in strata beneath the surface of the earth, several sources were exploited in early times. For example in Great Britain, jet was obtained from the Whitby beach area and shale from deposits in the Kimmeridge area.

Composition

Shale may vary considerably in composition. The Kimmeridge deposits include strata of clays, shales and the material known as Kimmeridge coal which is oil shale with a high bitumen content (Arkell, 1947). The organic extract of shale from Green River, Colorado was found to contain isoprenoid paraffins (12%), carotenoids (13%) terpenoids (20%) and steroids (20%) with a further 10% which seem to be the same types of compounds (Gallegos, 1971). The types of organic material are very similar to those discussed in the section on bitumens and asphalts.

Identification and interpretation of standard spectra

The similarity of the organic content of shale and jet to other bituminous materials and the variations in compostion between

shale strata from the same geographic location make the identification of materials such as jet or shale very difficult. An infrared spectrum was published (Gallegos, 1971) of the organic extract of the Green River shale. The infrared spectrum coupled with the nuclear magnetic resonance (NMR) spectrum were reported to give evidence for large quantities of branched chain alkanes and multiple ring constituents and small amounts of olefinic materials. The infrared spectrum was fairly simple and had strong bands located approximately at 2930, 2850, 1458, 1445, 1370 and 1360 cm^{-1} which are due to the C-H stretching and bending vibrations. The literature spectrum also exhibited weak bands near 1305, 1205, 1165, 970, 950, 930, 850, 810, 760 and 720 cm^{-1}. The diffuse reflectance technique has both advantages and disadvantages. It examines the whole sample and therefore gives a fingerprint which may be useful in identification of a material from a particular source. However, with the shale materials, the presence of inorganic materials may distort the spectra and cause alterations due to specular reflectance. The other difficulty is that only a few samples were obtained and a far larger collection of samples from a wider area is needed to make conclusive decisions about identity and provenance.

Two samples of dopplerite were obtained from the Institute of Archaeology mineralogical collection. The labels indicated that the materials came from Ireland and defined the dopplerite as secondary bituminous minerals formed as a humic acid gel by percolation in fissures of peat. The materials were classified with the shale and jet due to the similarities in the spectra.

Two samples of jet were obtained from different sources, one from the Whitby Museum and a second which was also said to be Whitby jet. Two samples of shale were also examined. One sample was a brown material which was thought to come from Kimmeridge and the second was obtained from Kimmeridge. The spectra of the Whitby jet were found to be very similar: the spectra of the two jet samples are shown in Figure 6.4. The spectra of the two shale samples (Figure 6.5) were observed to be different from each other and from the jet spectra. The dopplerite spectra were similar to each other with variations from the other types of material (Figure 6.6).

The jet spectra (Figure 6.4) are characterized by bands in the region of 2928 and 1446 cm^{-1} and a weak band in the region of 1375 cm^{-1}. These absorptions are due to the C-H stretching and

bending deformations which have been described earlier. The spectra are also characterized by absorptions near 1609 and 1510 cm^{-1} and near 824 and 754 cm^{-1} which are characteristic of aromatic compounds. The spectra also contain a weak absorption in the region of 3060 cm^{-1} which results from aromatic C-H stretches. The spectra contain a broad doublet centred near 3294 cm^{-1} which is indicative of O-H groups. The materials are unlikely to contain oxygenated compounds, so the bands are thought to result from hydrolysis of the samples over the period of time since they have been exposed to the atmosphere. The spectra contain a broad absorption centred at 1224 cm^{-1} and a weaker band at 1041 cm^{-1} which are probably due to the contribution of several compounds which are difficult to characterize.

The Kimmeridge shale spectrum (Figure 6.5b) contains the usual characteristic absorptions of the aliphatic C-H stretching vibrations at 2927, 2858 and 1379 cm^{-1}. The spectrum also exhibited bands at 1605, 781, 752 and 715 cm^{-1} which are indicative of substituted aromatic systems. The spectrum also contains a fairly intense band at 1705 cm^{-1} which probably results from the non-organic shale constituents. There is a

broad band centred at 1038 cm^{-1} with shoulders located near 1100 and 1180 cm^{-1} which are probably due to more than one component. The band at 1038 cm^{-1} may be representative of overlapping bands due to ring hydrocarbons which absorb in this region. For example, cyclohexane exhibits two absorptions in the regions 1005 - 925 cm^{-1} and 1055 - 1000 cm^{-1}. The spectrum contains evidence for the presence of calcium carbonate (calcite). The spectrum exhibits a strong absorption at 1450 cm^{-1} which corresponds to the band reported to occur at 1430 cm^{-1} in the literature (Miller and Wilkins, 1952). This band is broad and very intense and consequently masks the C-H deformation which is expected near 1465 cm^{-1}. The spectrum also contains a weak band at 2514 cm^{-1} and a medium, sharp band at 878 cm^{-1} which also correspond to those reported in the literature at 2530 and 877 cm^{-1} (Miller and Wilkins, 1952).

The spectrum of the brown shale (Figure 6.5a) which is suspected to be from Kimmeridge is somewhat different from that of the sample of known provenance. There is no evidence for the presence of calcite in the spectrum of the brown shale. The spectrum exhibits the bands expected of aliphatic hydrocarbons at 2889 and 1468 cm^{-1}, but the band expected in the region 1380 -

1370 cm^{-1} falls at 1345 cm^{-1} with a shoulder near 1360 cm^{-1}. The region between 1500 and 1200 cm^{-1}, which is dominated by the band at 1450 cm^{-1} with a weak band at 1379 cm^{-1} in the Kimmeridge shale spectrum, contains four sharp bands located at 1468, 1345, 1282 and 1241 cm^{-1} in the spectrum of the brown shale. There is a very broad absorption band with maximum intensities at 1104 and 1017 cm^{-1} which is probably the result of overlapping bands due to the complexity of the mixture. The spectrum contains a broad absorption which exhibits maximum intensity at 1606 cm^{-1} with a shoulder in the region of 1710 cm^{-1}, and weak bands at 844, 780 and 696 cm^{-1} which are indicative of aromatic compounds.

The dopplerite spectra are characterized by very broad absorptions (Figure 6.6). The two samples which are from different locations do not give identical spectra. There are similarities between the spectra which include a strong broad band centred at 3385 (IA3) and 3336 cm^{-1} (IA4), a very weak absorption near 2929 cm^{-1} in the spectrum of IA4 which appears as a shoulder on the broad band and is extremely weak in the spectrum of IA3. Both spectra exhibit a broad band with maximum intensity at 1613 cm^{-1} (IA3) and 1608 cm^{-1} (IA4) with a shoulder in the region of 1700 cm^{-1} which is similar to the region in the

spectra of the jet samples and in the brown shale spectrum. This absorption is probably due to the skeletal ring breathing mode in aromatic compounds. The spectra of the dopplerite samples also contain a weak absorption at 1511 cm^{-1} (IA3) and 1510 cm^{-1} (IA4) which could also result from skeletal ring breathing modes. The spectrum of IA3 has an absorption at 1429 cm^{-1} which has an extremely broad shoulder which masks the second absorption expected near 1480 cm^{-1}. The spectrum of IA4 has two bands located at 1431 and 1378 cm^{-1}, but the bands are fairly broad. The region between 1100 and 900 cm^{-1} is marked by three broad absorptions with maxima at 1086, 993 and 917 cm^{-1} in the spectrum of IA3 while the region in the spectrum of IA4 is also a very broad absorption with maxima at 1220, 1148 and 1064 cm^{-1}. The spectrum of IA3 is marked by a sharp absorption at 3621 cm^{-1} and has three weak absorptions located at 829, 753 and 695 cm^{-1}. In the spectrum of IA4, the absorptions are visible, but the strongest band is located at 754 cm^{-1}.

Identification of unknown samples

Eight black beads from a Roman cemetery site at Verulamium, St Albans (Verulamium Museum V7532, numbers 146, 166, 127, 149, 152, 164, 168 and 131) were sampled with silicon carbide paper. The

sample was removed from the side of the beads to protect the drill marks which are evident in the holes. The spectra obtained were found to be almost identical, indicating that the material for the beads was probably obtained from the same source. The spectra were characterized by absorptions in the ranges 2928 - 2927 cm^{-1}, 2860 - 2858 cm^{-1}, 1453 - 1438 cm^{-1} and 1379 - 1377 cm-1 in addition to a broad absorption in the region 1607 - 1596 cm^{-1} shoulders near 1700 and 1651 cm^{-1}, a shoulder which is apparent on the strong C-H band in the region of 3066 cm^{-1}, and bands at 887 - 886 cm^{-1}, 822 - 820 cm^{-1} 752 - 739 cm^{-1} and 707 - 694 cm^{-1} (Figure 6.7a). There is a broad band with maximum absorption near 1261 and 1216 - 1198 cm^{-1} which in addition to the other bands are characteristic of almost all of the bituminous materials which have been discussed. Visual comparison of the bead sample spectra with those of the standard spectra showed the jet spectra to be the most similar in general shape and intensity. The only major variation is that the strong band in the region of 1014 - 1001 cm^{-1} in the spectra of the bead samples is not evident in the jet spectra where a much less intense band occurs at 1041 cm^{-1}. Without extensive numbers of samples from various locations, it is difficult to make a definite

identification. However, a tentative identification may be made based on the evidence obtained thus far that the beads are made of jet as their sample spectra is more similar to those of the Whitby jet than those of the two shale samples. The spectrum of one of the samples (V7532 #127) is compared to the jet from Whitby museum (GS17) in Figure 6.7.

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Figure 6.1 Structures of the cholestane (tetracyclic) (I) and hopane (pentacyclic) (II) skeletons (Mills and White, 1987).

Figure 6.2 Diffuse reflectance FT-IR spectra of (a) glance pitch (IA5) from the Dead Sea, Jordan (Group I) (gsva0149) and (b) material purchased from a market in Ankara, Turkey (KA4) (gsva0261).

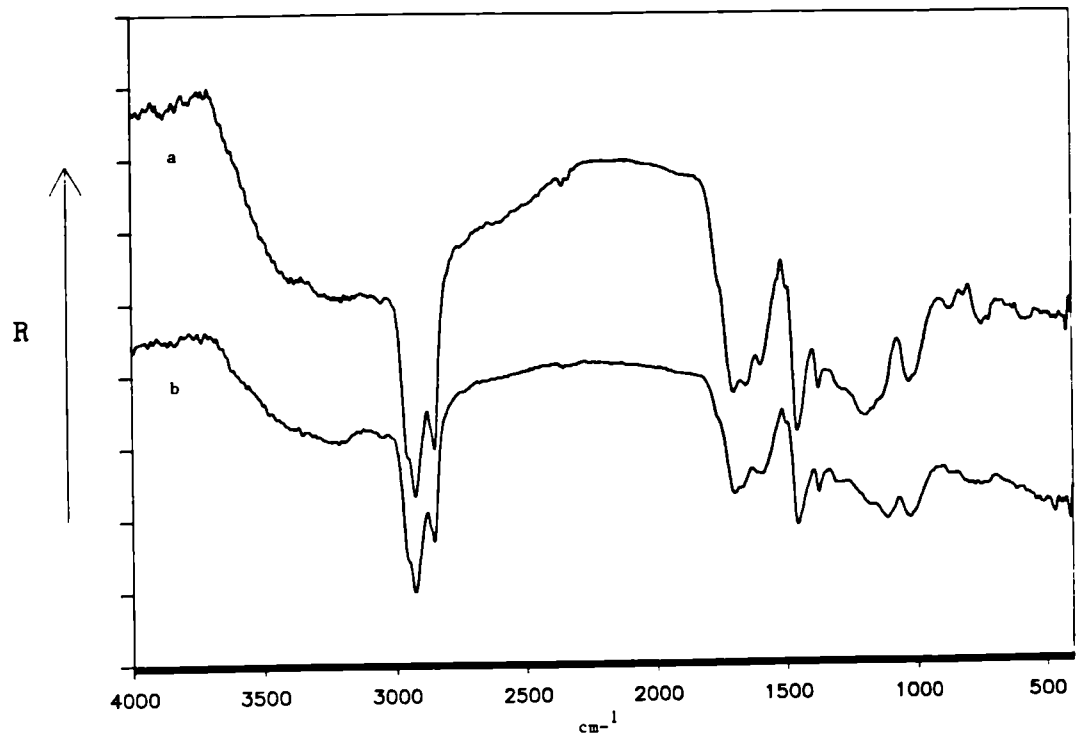

Figure 6.3 Diffuse reflectance FT-IR spectra of (a) asphalt (NJS24) from Khurbet Qumran, Jordan (Group I) (gsva0608) and (b) residue from flint sickle blade from Arpachiyah (KA1) (gsva0245).

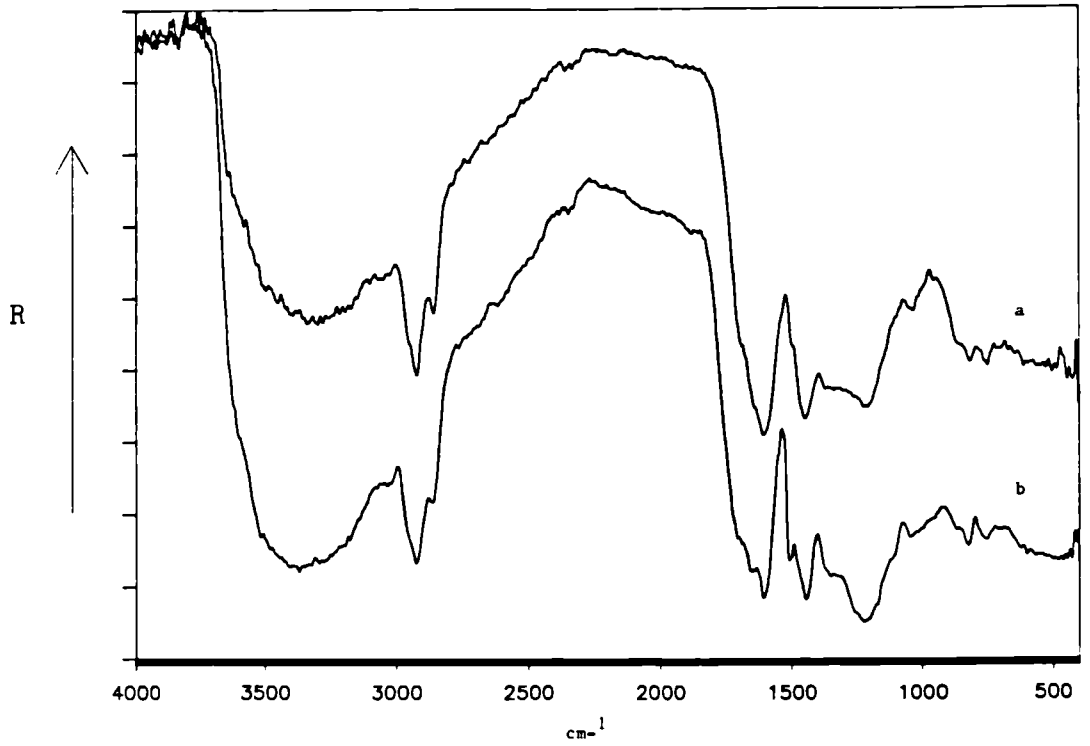

Figure 6.4 Diffuse reflectance FT-IR spectra of (a) jet from Whitby beach (NJS10) (gsva0230) and (b) jet from Whitby Museum (GS16) (gsva0517).

Figure 6.5 Diffuse reflectance FT-IR spectra of (a) brown shale thought to originate from Kimmeridge (GS15) (gsva0546) and (b) black shale from Kimmeridge (GS17) (gsva0547).

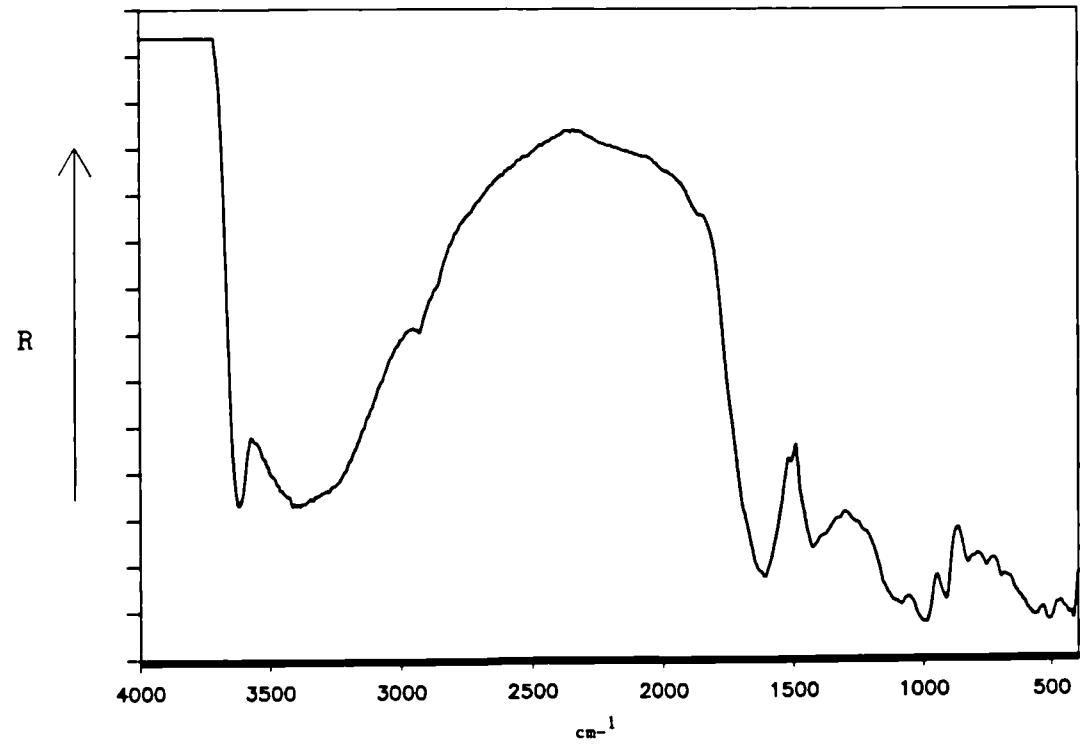

Figure 6.6 Diffuse reflectance FT-IR spectrum of dopplerite (IA3) from Garry Castle, County Westmeath, Althone (gsva0147).

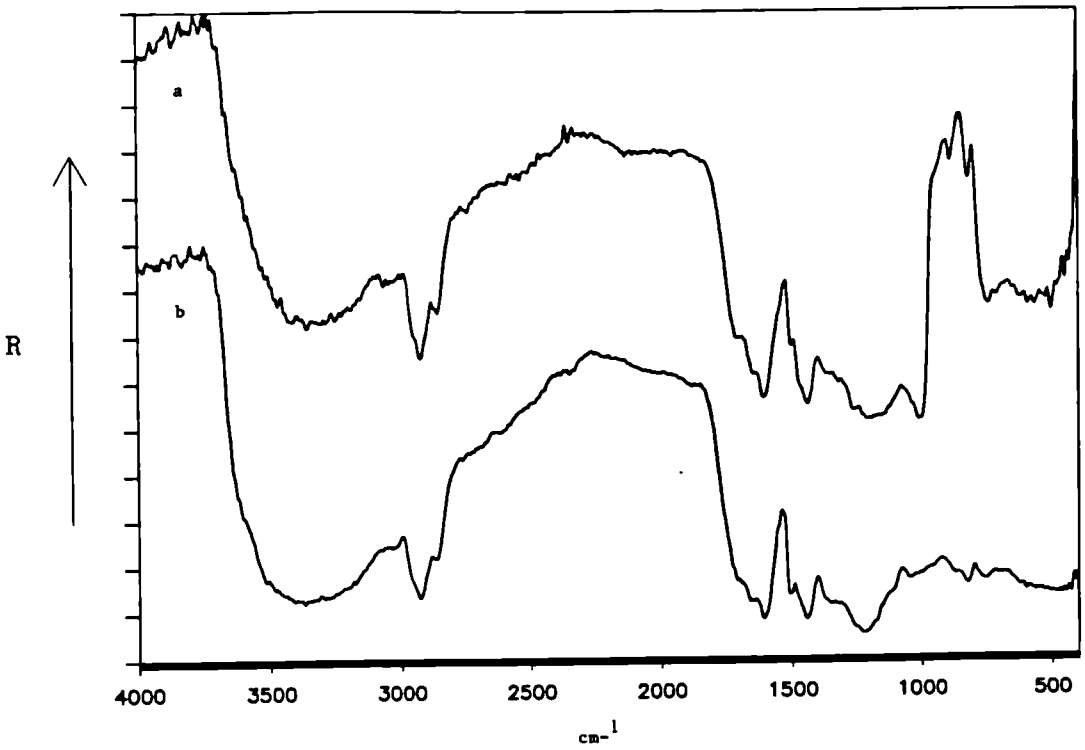

Figure 6.7 Diffuse reflectance FT-IR spectra of (a) black bead (DM3) found in cemetery at Verulamium, St. Albans (V7532 #127) (gsva0413) and (b) jet from Whitby Museum (GS16) (gsva0517).

TABLE 6.1

Frequency values and band assignments for bitumens and unknowns identified as bitumen

Group I cm-1	Group II cm-1	KA4 cm-1	KA1 cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
3295 - 3190(m)	3368 - 3174(va)	3180(sh)	3217(m,b)	O-H stretch	water	
* 2959(s)	* 2953(s)	2947(s)		C-H stretch	methyl group	2962 ± 10(s)
2933 - 2924(s)	2929 - 2923(s)	near 2920(s)	2928(s)	C-H stretch	methylene group	2926 ± 10(s)
2866 - 2855(s)	2869 - 2855(s)	near 2850(s)	2855(s)	C-H stretch	methylene group	2853 ± 10(s)
* 2730 - 2727(w)	* 2732 - 2727(w)	near 2730(w)	near 2730(sh)	unassigned		
	1706 - 1695(va)		1702(m)	unassigned		
* 1652 - 1647(va)	* 1660 - 1645(va)			skeletal ring stretch	aromatic ring	1650 - 1585(s) unsym. tri-substitution
				C=C stretch	C=C bond non-conjugated	1680 - 1620(va)
1605 - 1598(va)	1607 - 1598(va)	1600(m)	near 1600(m)	skeletal ring stretch	aromatic ring	1600 - 1560(w unless conjugated)
				C=C stretch	C=C bond phenyl conjugated	near 1625(s)
				C=C stretch	C=C bond, aliphatic conjugated	near 1600(s)
1464 - 1459(s)	1461 - 1457(s)	1465(s)	1460(s)	C-H asym. deformation	methyl group	1450 ± 20(m)
				C-H deformation	methylene group	1465 ± 20(m)
1379 - 1376(s)	1379 - 1377(s)	1378(s)	1379(m)	C-H sym. deformation	methyl group	1380 - 1370(s)
1209 - 1203(w)	* 1205 - 1185(w)	near 1210(b)	near 1200(sh)	skeletal vibrations	branched chain alkanes	see text
	1164 - 1143(w)			skeletal vibrations	branched chain alkanes	see text
			1119(s)	unassigned		

TABLE 6.1 contd.

Frequency values and band assignments for bitumens and unknowns identified as bitumen

Group I	Group II	KA4	KA1	Vibration	Functional group	Frequency range given in literature (1)
cm-1	cm-1	cm-1	cm-1			cm-1
1049 - 1018(w)	1043 - 1014(w)	1030(m)	1033(s)	ring deformation	cyclohexane	1055 - 1000(m)
* 958(w)	* 960 - 917(w)	near 950(sh)		ring deformation	cyclohexane	1005 - 925(m)
* 882 - 860(va)	* 879 - 871(va)	865(m)		C-H out-of-plane deformation	aromatic ring	900 - 860(m) one free H atom
* 820 - 813(va)	* 821 - 800(va)	812(m)		C-H out-of-plane deformation	aromatic ring	860 - 800(vs) para-substitution
* 772(w)				C-H out-of-plane deformation	aromatic ring	810 - 750(vs) meta-substitution
* 753 - 744(va)	758 - 743(va)	750(m)	754(w,b)	C-H out-of-plane deformation	aromatic ring	770 - 735(vs) ortho-substitution
				C-H out-of-plane deformation	aromatic ring	770 - 730(vs) mono-substitution
near 727(sh)		near 725(m)		C-H out-of-plane deformation	aromatic ring	710 - 690(s) mono-substitution

* Absorption is very weak or absent in some spectra.

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 6.2

Frequency values and band assignments for jet, shale, dopplerite, and unknown beads

Jet GS16 cm-1	Jet NJS10 cm-1	Shale GS15 cm-1	Shale GS17 cm-1	Dopplerite IA3 cm-1	Dopplerite IA4 cm-1	Unknown beads cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
				3621(sp)			unassigned		
3294(b)	3299(b)	3328(b)	3384(b)	3385(s,b)	3336(s,b)	3419 - 3310(m,b)	O-H stretch	water	
nr 3060(sh)	nr 3060(sh)	nr 3060(sh)	nr 3060(sh)			* 3066(w)	C-H stretch	aromatic ring	3070 and 3030(w)
2928(s)	2926(s)		2927(s)	nr 2920(sh)	2929(w)	2928 - 2927(s)	C-H stretch	methylene group	2926 ± 10(s)
nr 2850(w)	2861(m)		2858(s)			2860 - 2858(m)	C-H stretch	methylene group	2853 ± 10(s)
			2514(w)				calcium carbonate		2530(vw) (2)
nr 1700(sh)	nr 1700(sh)	nr 1710(sh)	1705(s)	nr 1700(sh)	nr 1700(sh)	nr 1700(sh)	unassigned		
nr 1650(sh)	nr 1650(sh)					nr 1651(sh)	skeletal ring stretch	aromatic ring	1650 - 1585(s) unsym. tri-substitution
							C=C stretch	C=C bond non-conjugated	1680 - 1620(va)
1609(s)	1610(s)	1606(s)	1605(m)	1613(s,b)	1608(s,b)	1607 - 1596(s)	skeletal ring stretch	aromatic ring	1600 - 1560(w unless conjugated)
							C=C stretch	C=C bond phenyl conjugated	near 1625(s)
							C=C stretch	C=C bond aliphatic conjugation	near 1600(s)
1510(w)	nr 1500(w)	nr 1500(vw sh)	nr 1500(vw sh)	1511(w)	1510(w)	nr 1504(w)	skeletal ring stretch	aromatic ring	1525 - 1475(va)
1446(s)	1452(s)	1468(s)		nr 1480(sh)		1453 - 1438(s)	C-H asym. deformation	methyl group	1450 ± 20(m)
							C-H deformation	methylene group	1465 ± 20(m)
			1450(s)	1429(s,b)	1431(s,b)		calcium carbonate		1430(vs,b) (2)
nr 1375(w)	nr 1375(w)	nr 1360(sh)	1379(w)		1378(s,b)	* 1379 - 1377(m)	C-H sym. deformation	methyl group	1380 - 1370(s)
		1345(s)					unassigned		

TABLE 6.2 contd.

Frequency values and band assignments for jet, shale, dopplerite, and unknown beads

Jet GS16 cm-1	Jet NJS10 cm-1	Shale GS15 cm-1	Shale GS17 cm-1	Dopplerite IA3 cm-1	Dopplerite IA4 cm-1	Unknown beads cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
		1282(s)					skeletal	branched chain	see text
nr 1260(sh)	nr 1260(sh)	1241(s)				nr 1261(sh)	vibrations	alkanes	
1224(s)	1226(s)				1220(s,b)	1216 - 1198(s)	unassigned		
			nr 1180(sh)		1148(s,b)		unassigned		
		1104(s,b)	nr 1100(sh)	1086(s,b)	1064(s,b)		unassigned		
1041(w)	nr 1040(w)	1017(s,b)	1038(s)	993(s,b)		1014 - 1001(s)	ring deformation	cyclohexane	1055 - 1000(m)
			916(w)	917(s,b)			ring deformation	cyclohexane	1005 - 925(m)
nr 880(w)	nr 880(w)		878(m)			887 - 886(m)	C-H out-of-plane deformation	aromatic ring	900 - 860(m) one free H atom
			878(m)				calcium carbonate		877(s,sp) (2)
824(m)	817(m)	844(m)	nr 820(sh)	829(w)		822 - 820(m)	C-H out-of-plane deformation	aromatic ring	860 - 800(vs) para-substitution
		780(w)	781(w)				C-H out-of-plane deformation	aromatic ring	810 - 750(vs) meta-substitution
754(w)	751(w)		752(w)	753(w)	754(w)	752 - 739(w)	C-H out-of-plane deformation	aromatic ring	770 - 735(vs) ortho-substitution
							C-H out-of-plane deformation	aromatic ring	770 - 730(vs) mono-substitution
nr 700(vw)	nr 700(vw)	696(w)	715(w)	695(w)	nr 690(vw)	694 - 707(w)	C-H out-of-plane deformation	aromatic ring	710 - 690(s) mono-substitution

* Absorption is weak in some sample spectra

1. Bellamy, 1975
2. Miller and Wilkins, 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

CHAPTER 7 RESINS AND RELATED MATERIALS

Resins

Source

Resin is the general term which is used for the exudate of many varieties of plants and trees. The sticky materials are not soluble in water and are produced as by-products of plant metabolism. They have been used by man since antiquity, primarily as adhesives, varnishes and binding media. The materials are found in both archaeological and art objects (Mills and White, 1987). The initial tree product is often referred to as an oleo-resin or balsam which may be distilled to produce turpentine as the distillate and rosin or colophony as the residue (Gettens and Stout, 1966).

Composition

Resins are composed of mixtures of complex chemical compounds. Little information was obtained on the structure of resins until the development of modern chromatographic methods which are capable of separating the various components. The primary components are terpenoids (Mills and White, 1977). Terpenoids are composed of isoprene building blocks. (The structure of isoprene is given in Figure 7.1.) Monoterpenoids are composed of

two isoprene units and contain 10 carbon atoms. Similarly, sesqui-, di- and triterpenoids are compounds which contain 3, 4 and 6 isoprene units and contain 15, 20 and 30 carbon atoms respectively (Mills and White, 1987). At normal temperatures, the C-10 and C-15 compounds occur in the liquid state and act as solvents for the C-20 and C-30 compounds which are solid. The di- and triterpenoids have not been found in the same resin and this criteria is used to classify the materials. However, the mono- and sesquiterpenoids may appear in the same resin (Mills and White, 1977; Mills and White, 1987).

One of the best known monoterpenoid mixtures is oil of turpentine which is the distillate of crude resin and widely used as a painting material and contains several monoterpenoid compounds. Many of the Pinaceae genera produce a similar monoterpenoid product, but the largest producers are the species of the Pinus genus. Thus, the other products are less abundant and more expensive. Also, essential oils which provide the characteristic odour of flowers and herbs are composed of oxygenated monoterpenoids (Mills and White, 1987).

Until recently, detailed knowledge of the chemical composition of various resins was not known. Although this type of information is now available, it is not of great use in analysis of art and archaeological samples. The reactions which occur over time alter the original composition and make a specific identification difficult. In some cases when a large amount of sample has been preserved or if the sample has not undergone extensive oxidation, the specific Pinus species may be identified. This is very rare. In some cases, the presence of a specific chemical compound may be used to identify a specific resin. For example, the presence of larixol and larixyl acetate indicates the presence of the Larch resin, Larix decidua Miller, commonly known as Venice turpentine, and only this resin and and Larix gmelinii have been found to have this composition. However, this type of analysis is dependent on an efficient separation technique. As with the bituminous materials, FT-IR presents the infrared spectrum of the entire compound and does not distinguish between various components. However, the resins as a group are characteristic and may be differentiated from other materials on the basis of the infrared spectra. Thus, a detailed analysis of the chemistry of resins is not appropriate in this thesis and only a general

outline is presented. A more complete summary of resin chemistry as it relates to art and archaeology is given by Mills and White (1977; 1987).

Diterpenoid resins

The principal sources of diterpenoid resins are Coniferales and the Leguminosae sub-family, Caesalpinioideae. The families of the Coniferales which produce resins which are believed to be the major sources for art and archaeology are summarized in Table 7.1 (Mills and White, 1987). Only the major resin producers are listed. Among the diterpenoid resins, there are several important skeletons which include the abietane and pimarane series which have three rings and the labdane series which have two rings and a side chain. The principal form of the materials contain the carboxylic acid functional group, although alcohol and aldehydes occur in small quantities. Examples are given in Figure 7.2 of laevopimaric, palustric, neoabietic and abietic acids which are abietadienes. The structures are very similar with variations in the position of the double bonds. The pimaradiene structures are similar to those of other series, but contain double bonds in different positions which may not be conjugated (Mills and White, 1977).

The most important labdane compound is trans-communic acid and others include cis-abienol, agathic acid, manool, lambertianic acid and pinusolide in addition to larixol and larixyl acetate (Figure 7.3). In the Leguminosae resins, the mirror-image structures or enamtiomers of the labdane series compounds are found. In these materials, the stereochemistry is reversed at the three asymmetric centers (Mills and White, 1977).

In summary, the resins of the Pinaceae are characterized by large quantities of the pimarane and abietane acid compounds. The Cupressaceae resins are composed primarily of labdane structures and those of the Araucariaceae contain a large amount of labdane compounds with smaller amounts of pimarane and abietane materials. As mentioned above, the Leguminosae resins are characterized by the presence of labdane structures (Mills and White, 1987).

Triterpenoid resins

The major sources of the triterpenoid resins are the tropical Dipterocarpaceae sub-family, the Dipterocarpoidaeae which are known as the dammars. The sub-family contains 15 genera with more than 500 species and the harder resins, known as dammars,

have become popular as picture varnishes and may possibly occur in conjunction with ethnographic and archaeological objects. The second important type is the resin known as mastic which is obtained primarily in the Mediterranean coast from Pistacia lentiscus L. (Anacardiaceae family). A resin is obtained from the tree known as P. terebinthus var. atlantica or P. atlantica which is found in Turkey, Cyprus and the Near East and this resin is known as Chian turpentine. Several resins are obtained from the Burseraceae family. The genera Canarium, Bursera and Protium produce resins which have been known as elemi resins. The Commiphora and Boswellia families produce the gum resins myrrh and frankincense which will be discussed in a later section (Mills and White, 1977; Mills and White, 1987).

The triterpenoids are usually tetracyclic or pentacyclic structures. The major tetracyclic compounds contain the dammarane or euphane skeletons (Figure 7.4). The dammarane and euphane structures are characterized by a ketone functionality or a hydroxyl group at position three and the side chain often contain double bonds and other functionalities. The major pentacyclic structures include the ursane and the oleanane compounds (Figure 7.4) and lupane and hopane series are found in

lesser quantities and are less important (Mills and White, 1977). The ursane and oleanane when hydroxyl substituted at position 3, are refered to as alpha- and beta-amyrin and often occur in the same resin (Mills and White, 1977).

It is not known from what specific source the dammar used in Europe and the United States comes, however it is thought to be from either the Hopea or Shorea species and it has been found to contain primarily dammarane skeleton structures and polymeric hydrocarbons. Mastic has been found to have a greater variety of consitituents which have not been fully examined. The compounds which have been found include the euphane skeleton acids and a few oleanane materials (Mills and White, 1987).

Ageing

As mentioned before, the composition of resins alters considerably with time. The structures of the abietane series which have been discussed differ by the location of the conjugated double bonds. The heating process causes alterations of the structure and the resulting product is composed of abietic acid with little or no laevopimaric acid. Also, as the materials age, the acids are converted by dehydrogenation to dehydroabietic

acid (Figure 7.2) The material, 7-oxodehydroabietic acid (Figure 7.2) is formed from dehydroabietic acid by autoxidation. The structure of the material contains a ketone functional group (Mills and White, 1977). The presence of the two degradation products has been detected by gas chromatography and gas chromatography/mass spectroscopy and used to identify the materials as being a pine resin (Mills and White, 1977; Mills and White, 1987).

The labdane compound trans-communic acid has a conjugated carbon double bond in the side chain which is susceptible to polymerization. This is also the case for other compounds in the series. Resins which contain large amounts of trans-communic acid are transformed over a period of time to polycommunic acid which is a polymer of low molecular weight.

Interpretation of standard spectra

A number of resins from the families listed in Table 7.1 were obtained from the Museum of Economic Botany, Kew, and the diffuse reflectance spectra were obtained of the original surface of the sample and from a freshly exposed surface. The resins analyzed in this study are listed in Table 7.2. The samples of the

natural surfaces of the conifer resins show a fair amount of detail and thus, the resins are not thought to have been heavily degraded. For the most part, the region between 1300 - 400 cm^{-1} shows evidence of overlapping due to the large number of components in the resins. However, some distinct bands are evident and quite a large amount of variation in the occurrence of bands which does not appear to be consistent within families. The spectra of the natural surfaces exhibit bands in very similar ranges and show a similar degree of variation. The frequencies of the various families for both natural and fresh surfaces are listed in Table 7.3. It must be stressed that there is a great deal of variation in the occurrence of the bands between the various samples. The spectra of the Hymenaea species, verrucosa and courbaril, show slightly less detail than the conifer resins. The mastic resin spectra, however, are marked by very broad, indistinct absorptions and a loss of detail in the region 1300 - 400 cm^{-1} in comparison to those of the conifer resins. There is even less detail present in the spectra of the natural surface samples.

It is difficult to make specific band assignments for extremely complex mixtures such as resins. Also, several bands in a

particular region may be due to the same functional group which is present in several different components of a mixture. However, several regions are characteristic for resins. The primary functional group which is present in most resins is the carboxylic acid group. This functional group which has been discussed in earlier sections is marked by the presence of bands in the region of 3000 - 2500 cm^{-1} for samples in the solid state. In this region, a broad band is observed as a shoulder on the high frequency side of the C-H stretching bands and a "satellite band" is observed in the region 2700 - 2500 cm^{-1}, usually near 2650 cm^{-1}. The group also contains a carbonyl group. The general range for absorptions due to this group for aryl acids is listed as 1700 - 1680 cm^{-1} and the range listed for alpha-, beta-unsaturated acids is 1705 - 1690 cm^{-1}. There are several other characteristic absorptions which include a weak band in the region of 1440 - 1375 cm^{-1} with a second, stronger band located in the region of 1300 cm^{-1} which are thought to result from a coupled C-O stretching vibration and an O-H in-plane deformation. Carboxylic acids are often marked by a second, more intense band which has been observed to occur at a lower frequency in the wide range 1320 - 1211 cm^{-1}. However, the band assignment has not

been fully elucidated. The group is also marked by a fairly intense, broad band in the region 950 - 900 cm^{-1} which is due to the O-H out-of-plane bending vibration (Bellamy, 1975).

Other functional groups which may contribute to the spectra are the ketone group and the hydroxyl group. The hydroxyl group is very polar in nature and forms hydrogen bonds with other polar materials. Intermolecular bonded O-H groups result in a broad, strong band in the region 3400 - 3200 cm^{-1} (Bellamy, 1975). The presence of O-H groups may cause a band with a higher frequency than would be expected for carboxylic acids alone. The ketone group which is attached to six-carbon rings results in absorptions in the range expected for open chain, aliphatic ketones, 1725 - 1705 cm^{-1}. The presence of alpha-, beta-unsaturation has been observed to lower the frequency range to 1684 - 1674 cm^{-1}. However, higher frequencies are observed in fused ring systems and this may counteract the shift caused by the unsaturation (Bellamy, 1975). Thus, carbonyl absorptions which have higher frequencies than would be expected for carboxylic acids may be the result of both types of functional groups.

The spectra of the resins may also be affected by the presence of carbon-carbon double bonds. The characteristic regions were discussed in the section on fatty acids and include 3040 - 3010 cm^{-1} for -CH=CH- C-H stretches and 3095 - 3075 cm^{-1} for terminal =CH2 groups and 1680 - 1620 cm^{-1} for the C=C stretches. The regions of 1310 - 1295 cm^{-1} and 970 - 960 cm^{-1} are characteristic of trans-substituted isomers and near 690 cm^{-1} are expected of cis-substituted compounds (Bellamy, 1975).

The resin spectra, in general, are marked by a broad absorption in the region 3500 - 3100 cm^{-1} (the ranges of values are listed for each family in Table 7.3). Often, the band has a maximum intensity near 3400 cm^{-1} which then runs into the C-H absorptions. The band appears as a shoulder on the C-H absorptions in only a few spectra. The band is probably due to the presence of both bonded hydroxyl stretches and carboxylic acid stretches. The resin spectra also contain a band or shoulder in the region of 2650 cm^{-1} which corresponds to the "satellite band" which is characteristic of carboxylic acids. The band tends to appear as a shoulder in the spectra of the Pistacia and in some of the resin sample spectra. The spectra are also marked by an absorption in the carbonyl region. In general, the

absorptions fall into the range listed for alpha-,beta-unsaturated carboxylic acids, 1705 - 1690 cm^{-1}, but in some spectra, the frequency value may be as high as 1719 cm^{-1}. The higher values agree with the range given for saturated, aliphatic acids, 1725 - 1700 cm^{-1}, also, the frequency shift may be caused by the presence of additional ketone groups.

In the spectra of both the fresh and natural surfaces of the conifer resins, bands are apparent which may be assigned to other characteristic absorptions in the carboxylic acid group. Bands are observed near 1400 cm^{-1}, 1300 cm^{-1} (except in the Pinaceae resins) and near 950 cm^{-1}. Also, in almost all spectra, a very intense band is observed near the region of 1280 - 1230 cm^{-1} with most occurring near 1240 cm^{-1}. Although these bands are not all apparent in every spectrum, they may be tentatively assigned to absorptions due to the carboxyl group.

In the Hymenea species, the fresh surface sample spectra exhibit bands in the regions 1266 - 1253 cm^{-1} and 944 - 942 cm^{-1}, however, the bands are less distinct in the spectrum of the natural surface of H. verrucosa where only a shoulder is apparent in the region of 1250 cm^{-1}. In the natural surface spectrum of

H. courbaril, bands appear at 1241 cm^{-1} and 949 cm^{-1}. There is less detail in the mastic spectra. In both the fresh and aged sample spectra (except the fresh P. terebinthus), a broad band is observed with a maximum intensity in the region 1194 - 1184 cm^{-1}. The bands near 960 cm^{-1} are only observed in the spectra of the fresh surfaces of the two P. lentiscus samples. The bands which are expected near 1400 and 1300 cm^{-1} are not apparent in any of the Hymenea or Pistacia spectra. The loss of these bands and the band near 960 cm^{-1} is probably due to the increased complexity of the resins which cause band overlap and subsequent masking of expected bands.

There is some evidence of the C=C group in some of the diterpene resin spectra. There are weak absorptions visible in the region 3080 - 3060 cm^{-1} in certain spectra which may be indicative of C-H stretches of carbon double bonds. However, the values fall slightly between the ranges of 3095 - 3075 cm^{-1} and 3040 - 3010 cm^{-1} given by Bellamy (1975). The spectra are also marked by weak bands or shoulders in the regions near 1600 and 1650 cm^{-1} which may be due to C=C stretching vibrations. These bands are not apparent in either the fresh or natural surface spectra of the Pistacia resins. The regions which are characteristic of C-H

deformations for double bond trans- structures, 1310 - 1295 and 970 - 960 cm^{-1}, are also characteristic for carboxylic acids and the assignments for regions which have been made may in fact include these absorptions as well. Many of the diterpenoid spectra contain a weak absorption near 700 cm^{-1} which may correspond to the C-H deformation in cis-substituted isomers which is expected near 690 cm^{-1}. None of the C=C characteristic absorptions occur in the triterpenoid Pistacia spectra.

The resin spectra are also characterized by absorptions which are typical of C-H stretches and deformations. The second absorption is centred near 2870 cm^{-1} in most of the resin spectra and sometimes appears as a shoulder on the lower frequency side of the stronger band in the region of 2940 cm^{-1}. The resin spectra are also characterized by two absorptions of approximately equal intensity in the region of 1467 - 1450 cm^{-1} and 1388 - 1365 cm^{-1} which may be assigned to the C-H deformations.

Identification of unknown samples

When samples from archaeological contexts were examined, it became evident that the amount of detail which was observed in the resin standards was not retained in aged samples. This was

not surprising. However, the spectra retained a sufficient number of characteristic absorptions of carboxylic acid to be classified as resins. Also, the resin spectrum has a characteristic shape which is also indicative (see Figure 7.5). Twenty samples from various provenances were identified as resins and the ranges of frequencies which were observed to be characteristic of resins are listed in Table 7.4. The frequency values were found to be somewhat similar to those of a commercial sample of colophony which have been included for comparison. In addition to the samples which were identified as resins, a further twelve samples were tentatively assigned as resin mixtures. The spectra contain bands which are indicative of the carboxyl group, but the presence of other interfering bands from admixed materials or degradation products of the resin itself has obscured the spectra. Thus, the identification of these samples is merely tentative. The differentiation was made by visual and consequently subjective means. The details of the individual samples are listed at the end of the section.

The samples which were identified as resins are characterized by a broad absorption with maximum intensity in the region 3437 - 3221 cm^{-1}, a weak shoulder in the region 2641 - 2627 cm^{-1}, a

strong band in the region 1726 - 1701 cm^{-1} and a band in the region of 985 - 958 cm^{-1} which are characteristic of carboxylic acids and have been discussed in detail. The spectra are also marked by a very intense, but somewhat ill-defined absorption with maximum intensity in the region of 1215 - 1179 cm^{-1}. In a few cases, a second absorption was observed in the region of 1138 - 1132 cm^{-1} or 1238 - 1223 cm^{-1} and in two samples, the maximum absorption occurred in the region of 1236 - 1223 cm^{-1} instead of 1215 - 1179 cm^{-1}.

The spectra are also marked by a broad band at 1050 - 1039 cm^{-1} which appears in almost all of the reference resin spectra, but has not been assigned to a specific functional group. The sample spectra also contain two bands of fairly equal intensity in the regions of 1463 - 1450 cm^{-1} and 1387 - 1379 cm^{-1}.

The remaining absorptions which have been noted in the standard resin spectra do not occur consistently in the sample spectra. Weak bands are evident in some of the spectra in the region 3084 - 3071 cm^{-1} and 1610 - 1607 cm^{-1} which may be due to C=C structures. Also, the band in the region 985 - 958 cm^{-1} may be due to both the O-H out-of-plane deformation in carboxylic acids

and the C-H deformation due to trans-substituted ethylenic bonds. A weak band is apparent in some spectra near 1420 - 1416 cm^{-1} which is due to carboxylic acids, and a few spectra contain an absorption in the region 708 - 695 cm^{-1} which may be representative of cis-substituted isomers of C=C compounds. However, it must be noted that the region 1300 - 400 cm^{-1} is marked by only a few broad maxima with very weak bands in the region 900 - 400 cm^{-1}. An area of absorption is evident in the region of 769 - 747 cm^{-1} for some of the samples. As can be seen in Table 7.4, there is a great variation in the occurrence of absorptions in this region.

In general, the sample spectra are marked by a very broad band near 1200 cm^{-1} and the carbonyl band is also observed to become broader in addition to the slight shift to higher frequencies. This may be explained in part by the increasing complexity of the aged material. The broad absorption near 1200 cm^{-1} is probably due to a variety of absorptions which overlap The production of 7-oxodehydroabeitic acid in pine resins would result in the presence of ketone groups which may affect the shape and frequency of the carbonyl absorption. Also, there is a general loss of detail in the region 1300 - 400 cm^{-1} which is the result

of the great complexity of the mixture and has been described by Mills and White (1987).

The spectra of the materials which were tentatively assigned to resin mixtures were identified on the basis of presence of a broad band with a maximum intensity in the region of 3544 - 3229 cm^{-1}, a fairly weak shoulder on the lower frequency side of the C-H stretching vibration bands in the region of 2650 cm^{-1}, a strong band with maximum intensity in the region 1744 - 1706 cm^{-1}, a broad band with maximum intensity in the region of 1217 - 1174 cm^{-1} (some maxima are located between 1126 and 1125 cm^{-1}) and a band in the region 1076 - 1039 cm^{-1}. The remaining bands are variable in occurrence and the region between 950 - 400 cm^{-1} is very indistinct.

A sample was obtained from the non-reflecting side of a Chinese bronze mirror (Victoria and Albert Museum, FE87 1982) which was produced in Huzhou. A small amount of sample, which formed a black particulate inlay on the surface, was removed using a scalpel and rubbed on silicon carbide paper. The resulting spectrum was observed to resemble a resin spectrum upon visual examination and the computerized search selected the spectrum of

Pinus massoniana fresh surface as the closest match. The resin sample spectrum exhibited a greater degree of detail in the region 900 - 400 cm^{-1} than has been observed for other resins (Figure 7.5). However, the identification of the resin to a specific species must be treated with caution due to the similarity of the various resin spectra to each other. Also, no references have been found on the exploitation of P. massoniana. (Rupert Hastings, Museum of Economic Botany, Kew, personal communication). It is most probable that the sample is some sort of conifer resin which is native to China.

A second example illustrates the danger of making a precise identification based on the infared spectra of resins. A sample of material incorporated into the embalmed internal organs was obtained from the tomb of Djehuty Nakht located at Deir el Bersheh (XI dynasty). The spectrum of the material was observed to be a resin and the computer search suggested either the spectra of Juniperus phoenicia or Pistacia lentiscus as the closest match. However, the sample was characterized by gas chromatography/mass spectroscopy and both dehydroabietic acid and

7-oxodehydroabeitic acid were identified which indicated the presence of a pine resin (R. White, personal communication).

Unknown sample information

Resins

RK3 Sample taken of light brown residue/old repair from base of Chinese bronze vase, possible sealant. Provenance - unknown. Date - 12th - 13th century. Victoria and Albert Museum Far Eastern Department 121-1876.

RK4 Black particles on reverse of Chinese bronze mirror. Provenance - Huzhou. Date - unknown Far Eastern Department, Victoria and Albert Museum, FE87 1982.

MFA2a Black funerary resin?/residue from coffin of Nesptah. Provenance - unknown. Date - XXII - XXVIth dynasty Boston Museum of Fine Arts 72.4838.

MFA2b as for MFA2a sample taken with silicon carbide paper.

MFA3b Black resin from pectoral. Provenance - unknown. Date - Late period Boston Museum of Fine Arts 72.769.

MFA4 Black resin from embalmed internal organs. Provenance - Tomb of Djehuty Nakht, Deir el Bersheh. Date - XIth dynasty Boston Museum of Fine Arts.

MFA8 Black residue from back of shawabti of Merneptah. Provenance - unknown. Date - unknown Boston Museum of Fine Arts W29. Sample taken with silicon carbide paper.

MFA10 Yellow ?resin sample with aromatic odor. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts, Meyer Collection, no number.

MFA15 Sample of surface coating over painted design on dummy stone jars. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts 72.4268.

MFA18 Sample of black ?resin from back of gilded bracelet of Nefetari. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts 04.1955.

MFA20 Red residue from black Egyptian coffin. Provenance - unknown. Date - Middle Kingdom. Boston Museum of Fine Arts no number.

NJS11 Sample of adhesive used to hold inlays in gold relic box. Provenance - Gandhara region. Date - 1st - 2nd Century, A.D. Institute of Archaeology conservation laboratory number 3900.

AH1 Sample of orange residue from Egyptian textiles. Provenance - unknown. Date - unknown. Insitute of Archaeology conservation laboratory number 6108 via Petrie Museum.

KA7 Ethnographic knife with black ?resin handle. Provenance - central Australia. Date - unknown. Institute of Archaeology collection 52/1972 LP.4251. Sample compared to spectrum of hafting material composed of spinifex resin prepared by Aboriginals. Sample taken with silicon carbide paper.

SMC1 Sample of varnish from surface of Egyptian coffin lid described as uneven brownish/reddish varnish. Provenance - unknown. Date - ?XXI - XXIIth dynasty. Aberdeen University Anthropological Museum collection, via Scottish Museums Council SMC A194.

MS16 Golden yellow, brittle residue from model alabaster (?) cylinder jar. Provenance - unknown. Date - Old Kingdom (?). British Museum Egyptology Department 4481.

MS23 Golden orange, dry residue from alabaster (?) model one handled jar Provenance - unknown. Date - unknown. British Museum Egyptology Department 4567.

MS39 Reddish-brown, shiny, brittle residue with aromatic odour from small alabaster (?) cylinder jar with lid. Provenance - Kahun. Date - Middle Kingdom (XIIth dynasty). University College London Petrie Collection 7318.

MS40 as for MS39

MS41 Red-orange, sticky residue which appears dark brown on the surface from small alabaster (?) cylinder jar inscribed with titulary. Provenance - Hatshepsut Deir el Bahari foundation deposit. Date - New Kingdom (XVIIIth dynasty). University College London Petrie Collection 15862.

MS42 as for MS41, sample taken of dark material on surface.

Resin mixtures

IG1 Sample of resin used to hold stone blades in ethnographic adze, traditional design with chair spindle used in place of wooden shaft. Provenance - unknown, probably central Australia.

Date - unknown - probably late 19th to early 20th century. Ian Glover, Institute of Archaeology, Prehistory Department.

NJS14 Sample of residue from inside wooden hilt. Provenance - unknown. Date - unknown. Institute of Archaeology Department of Conservation laboratory number 1593.

MS31P Black/brown, friable residue from ceramic cylindrical jar with narrowing mouth. Provenance - Gebelain. Date - New Kingdom (late XVIIIth dynasty). British Museum Department of Egyptology 22198.

MS34P Black, friable residue from pottery brownware globular jar with white slip. Provenance - Buhen. Date - Middle Kingdom. British Museum Department of Egyptology 65686.

MS36P Brown/black, brittle residue form large ceramic globular jar with two small lugs on shoulders. Provenance - Tell Nebesheh. Date - Late Period (XXVIth dynasty). British Museum Department of Egyptology 22354 (166A).

MS38P Brown, powdery residue from large ceramic amphora with stippled lines and Hieratic inscription. Provenance - unknown. Date - unknown. British Museum Department of Egyptology. 30334.

MS34 Black, gritty residue from large alabaster (?) cylinder jar. Provenance - unknown. Date - unknown. British Museum Department of Egyptology 29866.

MS43 Medium brown, powdery residue from alabaster (?) cylinder jar with lid, both inscribed with titulary. Provenance - Hatshepsut Deir el Bahari foundation deposit. Date - New Kingdom (XVIIIth dynasty). University College London Petrie Collection 15863.

MFA7 Sample of orange resin and possibly some orpiment from beard. Provenance - ? Date - ? Boston Museum of Fine Arts 72.4798.

MFA9 Black contents from Egyptian alabaster jar. Provenance - unknown. Date - Old Kingdom. Boston Museum of Fine Arts 04.1887. Sample taken with silicon carbide paper.

MFA11 Red ?resin sample with aromatic odor. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts, Meyer Collection, no number.

Amber

Source

Amber is a fossil resin. Although 'fossil' resin has not been well defined, it refers to material which has existed for a very long period of geological as opposed to historical time. The material has been subjected to pressure and weathering from water and soil. The principle source for Baltic amber is the Eastern coast of the Baltic sea (modern day Poland and Lithuania). It has been found on other Baltic country coasts and on the Eastern shore of England as well as near the region of the Dnieper River and the Black Sea. In addition to the Baltic amber, smaller deposits have been found throughout Europe including Sicily, Rumania and Spain. The mineralogical name for Baltic amber is Succinite (Beck et al, 1965; Mills and White, 1987).

The source of the resin has long been credited to an extinct conifer species which was named Pinus succinifera, however, amber is not similar to modern resins from the Pinus family. However, recent research has shown that the chemical structure of amber is more similar to resins of the Araucariaceae species (Mills and White, 1987).

Amber was prized by early cultures and amber artifacts have been found in many grave sites from Neolithic times. The provenance of amber artifacts found in Europe, Baltic or non-Baltic, has been an important question for many years and was one of the first applications of scientific research in archaeology (Beck et al, 1965).

Composition

Baltic amber

Amber has a non-crystalline structure and is not very soluble in organic solvents. Amber is about 20% soluble in ether. The ether soluble fraction has been examined by gas chromatography and found to have a characteristic chromatogram containing several hundred components (Mills and White, 1987). The insoluble portion has been found to be a high molecular weight, crosslinked polymer. The structure is similar to a natural alkyd resin formed by the esterification reaction of a polyvalent alcohol and a dibasic acid (Mills and White, 1987). The amber contains a communic acid/ communol copolymer which acts as the polyvalent alcohol and succinic acid which is the dibasic acid. The structure is similar to that of kauri resin which contains

the copolymer of communic acid and communol. Amber also contains free carboxylic acid groups (Mills and White, 1987).

Other ambers

There has been very little analysis performed on other fossil resins (Mills and White, 1987).

Interpretation of standard spectra

Literature values

As mentioned above, Baltic amber may be identified by gas chromatography of the ether-soluble components (Mills and White, 1987). In addition, infrared spectroscopy has been used extensively to establish the provenance of European amber (Beck et al., 1965). The band assignments published by Beck have been made on the basis of almost 600 spectra of amber from Baltic and non-Baltic regions (Beck et al., 1965). It is emphasized in the article that that it is not possible to make very specific functional group assignments for spectra of natural products such as amber. The composition of this material is complex and there are many structurally similar components which result in broad bands and shoulders. The study also mentions that a wide range of frequency values (20 - 50 cm^{-1}) and intensities were observed

between different spectra of the same sample. Larger variations in frequency were observed for different samples from the same geological source (Beck et al., 1965).

The amber spectra in the literature (Beck et al., 1965) are marked by absorptions due to C-H, C=O, C-O and O-H bonds. The spectra contain absorptions due to C-H stretches and deformations which fall in the expected frequency ranges for methyl and methylene groups (Table 7.5). The presence of C=C bonds are suggested by the bands near 3095 and 885 cm^{-1}.

The broad band observed in the range 1770 - 1695 cm^{-1} is assigned to the C=O stretching mode due to both ester and ketone functional groups. Differences in the shape of the bands suggest that the material is a mixture of several different esters and ketones (Beck et al., 1965). The range for this band also includes the C=O absorption in carboxylic acids (Table 7.5) (Bellamy, 1975). The bands in the region 1250 - 1100 cm^{-1} are characteristic of the C-O stretching vibration in esters and are discussed below.

The broad band in the region 3700 - 3100 cm^{-1} is representative of various kinds of hydroxyl groups (Beck et al., 1965) including

those in carboxylic acids (Bellamy, 1975). The band near 1640 cm^{-1} is normally assigned to the O-H deformation. However, both the O-H vibrations increase in intensity with prolonged grinding time which indicates that amber is sensitive to reactions with water and/or oxygen in the air (Beck et al., 1965). The presence of the broad band in the region 3700 - 3100 cm^{-1} and a shoulder in the region of 2650 cm^{-1} indicate the presence of carboxylic acids (Table 7.5) (Bellamy, 1975).

The region between 1250 - 1100 cm^{-1} has been observed to be characteristic of Baltic amber. Absorptions in this region are due to the C-O stretching vibration in the ester group (Bellamy, 1975). The spectra of Baltic amber exhibit a broad, horizontal absorption between 1250 and 1175 cm^{-1} which appears as a shoulder on a band near 1150 cm^{-1}. The band near 1150 cm^{-1} has been assigned to saturated aliphatic esters (Beck et al., 1965; Bellamy, 1975). These bands have not been observed in the spectra of amber from European non-Baltic locations which show great variation in the region. The pattern has been observed in some spectra of ambers from the North American continent (Beck et al, 1965).

In some sample spectra, the horizontal absorption is not evident and a shoulder with what is described as a negative slope is apparent which slants downwards to the right. The cause given for this variation is that exposure to air will cause new C–O bonds to be formed which will absorb in the same region, but not in the identical area which would result in a change of shape of the broad band in the region (Beck et al., 1965).

The Baltic amber spectra also contain a band in the region of 885 cm^{-1} which has been assigned to the C-H out-of-plane deformation of a terminal olefin group. It is thought that the structure may be CR1R2=CH2. It has been suggested that the band may result from an exocyclic double bond on a agathic acid diterpene derivative (Beck et al., 1965).

The band near 885 cm^{-1} is affected by oxidation. The band appears as a shoulder in some spectra. It is apparent in all Baltic amber spectra obtained by Beck et al. (1965), and may be used to differentiate, to a certain extent, between European non-Baltic fossil resins (Beck et al., 1965).

Reference sample information

For this thesis, three samples of mineralogical amber were obtained. Two specimens were thought to be from Russia (LA1 yellow opaque, LA2 transparent orange) and a third was reported to be from Denmark (LA3). The locations suggest that the ambers are of Baltic origin, but the lack of precise provenance limits the validity of the samples. The sample from Denmark seems to have been cut from a larger piece, the inside section was an opaque yellow which was surrounded by a red crust. Diffuse reflectance spectra were obtained of both the centre and the crust.

Interpretation of standard spectra

The resulting infrared spectra correspond very closely to that described by Beck et al. (1965) and Mills and White (1987). The region between 1300 - 1100 cm^{-1} which has been described as characteristic for Baltic amber is clearly evident in all four sample spectra. The shoulder from 1250 - 1200 slants downwards which indicates that all of the samples have undergone some oxidation. In the spectrum of the weathered crust (LA3), the bands at 1028 and 888 cm^{-1} are somewhat masked by other absorptions near 950 cm^{-1} and a multiplet occurs with bands near

850, 830 and 805 cm^{-1} which are not apparent in the other spectra. The frequency values are compared to those given by Beck et al. (1965) in Table 7.5.

Identification of unknown samples

Unknown sample information

Two examples of archaeological amber artifacts were also examined. The first was an ochre stained object from a gravesite in Lieto, Finland (KM 19727: 465) (Airola, 1980). The sample was removed from the surface and no additional treatment was performed. The second object was a bead found during an excavation at High Down Hill, Sussex (1988.459 136). The outer surface of the bead was sandy in appearance and did not resemble amber. The bead was broken during excavation and the interior was observed to be a transparent red material thought to be amber. Spectra were obtained of both the interior and the exterior of the object.

Interpretation of unknown sample spectra

The spectrum of the amber from Lieto was very similar to those obtained for amber in this study and those which have been published (Beck et al., 1965; Mills and White, 1987). The band

in the region of 890 is very weak in relation to the other bands in the spectrum. However, there are no serious interferences due to the ochre. In particular, the characteristic region 1300 - 1100 cm^{-1} is not affected.

The spectrum of the High Down Hill bead interior is also very similar to those published in the literature including the characteristic region 1300 - 1100 cm^{-1}. The spectrum of the bead exterior, however, gives indications of contaminants. The spectrum is marked by weak bands at 2514 and 1794 cm^{-1}, a very strong, broad band with maximum intensity at 1451 cm^{-1}, a sharp band at 876 cm^{-1} and a weak band at 713 cm^{-1} which are characteristic of calcium carbonate (Miller and Wilkins, 1952). The region 1300 - 1100 cm^{-1} is somewhat obscured. The band at 1162 cm^{-1} is present but the broad shoulder between 1260 and 1200 cm^{-1} is not present. A steep shoulder is seen with a weak absorption near 1250 cm^{-1}. Also, the band at 1032 cm^{-1} is more intense than the band at 1162 cm^{-1} and may also be due to an inorganic constituent. The frequency values observed in this study are compared to the other ambers and the values given by Beck et al. (1965) in Table 7.5.

Shellac

Source

Lac is produced by the insect, Laccifer lacca Kerr (Family: Lacciferidae Cockerell) which is native to India (Wadia et al, 1969). The insects infest host trees and secrete the substance on the twigs and branches. The material is retrieved by scraping the stick-lac from the branches. The composition of lac is believed to be related to the type of host tree and the major tree is the Butea monosperma Lamk (Mills and White, 1987).

The major application of shellac is as a varnish material for a variety of objects and it was widely used in early conservation practice as an adhesive and for mending broken pottery (Mills and White, 1987).

Composition

Structure of fresh shellac

The raw material, known as stick lac, is processed by mechanical crushing, sieving and washing in water to remove tree and insect debris and this material is referred to as seedlac. Further purification is used to give various grades of shellac of commerce (Wadia, et al, 1969). The stick-lac is composed of 6 -

7% wax, 4 - 8% colouring matter, 70 - 80% resin and the remaining material consists of insect remains, water and other extraneous matter such as woody material (Wadia, et al, 1969).

The composition of the lac resin has been elucidated only in the past twenty years. It is known to be a polyester material formed from certain hydroxy acids (Wadia, et al, 1969). The identity and structure of two of the acids were established as aleuritic acid and shelloic acid (Figure 7.6). Further work estabished the identity of butolic acid (6-hydroxytetradecanoic acid) and jalaric acid which is a monobasic dihydroxy acid with an aldehyde functional group as components of lac resin (Wadia, et al, 1969). Jalaric acid is an alicyclic acid which is a derivative of the sesquiterpene cedrene (Mills and White, 1987). Other compounds isolated (Wadia et al, 1969) included epishellolic acid and epilaksholic acid and their epimers, shellolic acid and laksholic acid. The acids are very similar in structure to jalaric acid (Figure 7.6). In epishellolic and shellolic acids, the aldehyde functionality is replaced by a carboxyl group. In epilaksholic and laksholic acid, it is replaced by a hydroxymethylene group (Wadia, et al, 1969). The four acids are formed when jalaric acid is treated with 20% alkali for 10 days (Wadia, et al, 1969)

and they may actually be products of the alkali saponification treatment. Jalaric acid may also be autoxidized to epishelloic acid as the aldehyde functional group is susceptible to conversion to the carboxylic acid (Mills and White, 1987). Jalaric acid is thought to be the primary acid (Wadia, et al, 1969).

A second primary acid was identified as laccijalaric acid which was found to be a derivative of the cedrene sesquiterpenoids, and structurally very similar to jalaric acid with the primary hydroxyl group replaced by a methyl group (Singh, et al, 1969). Derivatives of laccijalaric acid similar to those mentioned above for jalaric acid were isolated. These derivatives include laccishellolic acid and laccilaksholic acid in which the aldehyde group is replaced by a carboxylic acid group and a hydroxymethylene group respectively and their epimers. However, it was not possible to isolate these derivatives in lac which had been subjected to a short (5 hour) period of saponification. This fact led the workers to conclude that the laccijalaric acid is the primary acid of the series in the resin (Singh, et al, 1969). The compounds are probably formed as artefacts during the

saponification, however, epilaccishallolic acid may be formed as an autoxidation product (Mills and White, 1987).

The resin component may be separated into "hard" and "soft" fractions by ether extraction as the hard resin is insoluble in ether (Khurana, et al., 1970). The hard resin was used to determine the probable structure of lac resin. The material is termed pure lac resin (Khurana, et al., 1970) and the workers concluded that the polyester molecule should contain four terpene acid groups and four aleuritic acid units. The terpene acid seems to be mainly jalaric acid. The molecular weight of the theoretical model is 2210 which is very close to that of the molecular weight experimentally obtained for the pure lac resin, 2095 ± 110. The proposed structure is given in Figure 7.7 (Singh, et al., 1974b). The proposed sequence is an average of the possible constituents (Mills and White, 1987). The soft resin fraction was found to consist primarily of dimer acid esters composed of aleuritic acid and a sesquiterpene compound (Singh, et al., 1974a). It has been suggested that the pure lac resin and the soft resin are fractions of a mixture of oligomers with a range of molecular weights (Mills and White, 1987).

Effects of ageing

Aldehydes are susceptible to oxydation and the aldehyde groups in shellac are converted to carboxylic acid groups over time. There are also a large number of free hydroxyl groups which are susceptible to further esterification. This would result in cross-linking and an increase in the average molecular weight. The process is thought to continue in shellac coatings. There has been little study of aged shellacs, but it has been observed that shellac is less soluble in alcohol over time (Mills and White, 1987).

Identification and interpretation of standard spectra

There is a chemical test for the identification of shellac (Vollman, 1957). Lac contains erythrolaccin of which traces are still present in bleached or decolourized shellac. Erythrolaccin forms a violet coloured salt when reacted with alkali. In decolourized shellacs, the colour ranges from pink to light brown in chlorine bleached material. However, the recommended procedure (Vollman, 1957) requires that the sample be soluble in ethanol which may be a problem with old samples.

Analysis of lac with gas chromatography is difficult. The reaction of jalaric acid with diazomethane is complicated and produces a number of products (Wadia, et al., 1969; Upadhye, et al., 1970). The hydroxy acid methyl esters were observed to produce multiple peaks indicating decomposition (Upadhye, et al., 1970). However, several old samples have been characterized using gas chromatography (Mills and White, 1987).

Shellac may be identified by the infrared spectrum (Mills and White, 1987). Five samples of lac were analysed, one of natural stick-lac and four of commercial lac including a sample of bleached shellac. The spectra were very similar (Figure 7.8a), with differences in the region of 800 - 400 cm^{-1} which may be due to the cross-linking which occurs as a result of age. The samples are of indeterminate age, a certain amount of ageing is thought to have occurred. The carbonyl absorption in the stick lac spectrum is more broad with three shoulders in the regions of 1640, 1610, and 1560 cm^{-1} and a slight band near 1510 cm^{-1} and resembles that in the spectrum of one of the commercial shellacs (BM1) in the region of 1640 - 1600 cm^{-1}. The shoulders in the spectrum of the crude material occur in characteristic aromatic regions and are probably due to the dyestuff still present in the

material. The other three spectra have bands at approximately 1715 and 1640 cm^{-1} with a slight shoulder on the band at 1640 cm-1. The region between 1500 and 900 cm^{-1} is very characteristic for shellac, however, in the spectrum of one of the commercial shellacs, the relative intensities are affected and the band in the region of 1140 cm^{-1} is much weaker and more narrow. Also, the band in the region of 1200 cm^{-1} falls at 1235 cm^{-1} which is somewhat beyond the range.

The spectra are characterized by absorptions in the regions of 2923 - 2933 cm^{-1} and 2854 - 2858 cm^{-1} which are due to C-H stretching and 1464 - 1469 cm^{-1} and 1375 - 1377 cm^{-1} which result from C-H bending deformations (Bellamy, 1975).

The spectra exhibit a broad absorption in the region of 3326 - 3421 cm^{-1} in the hydroxyl region. The spectra of solid carboxylic acids give rise to a broad absorption with a series of minor peaks in the range 3000 - 2500 cm^{-1}. The bands are usually partially superimposed on C-H absorptions (Bellamy, 1975) leading to the effect described by Mills and Plesters (1963). The proposed structure also contain a large number of hydroxyl groups which give rise to absorptions in the hydroxyl region.

The OH groups are very polar and will bond with other OH groups. The range of values for polymeric intermolecular bonds of alcohols is 3400 - 3200 cm^{-1} and is very broad (Bellamy, 1975). The band in the sample spectra is probably a combination of both types of vibrations.

The absorption in the carbonyl region is due to several sources. The proposed structure (Figure 7.7) is primarily a polyester with aldehyde, hydroxyl and carboxylic acid groups. It is thought that the aldehydes are oxidized to carboxylic acids and that some of the hydroxyl groups may form further esters (Mills and White, 1987). It is probable that the spectrum reflects the presence of esters and carboxylic acids. The range of values for the carbonyl stretch in aryl esters is given by Bellamy as 1730 - 1717 cm^{-1} and the value for aryl aldehyde C=O stretch is 1715 - 1695 cm^{-1}. The range for the carbonyl absorptions in aryl carboxylic acids is 1700 - 1680 cm^{-1}. The range observed in the spectra obtained in this study is 1713 - 1717 cm^{-1} and is thought to be due to a combination of carboxyl and ester carbonyl absorptions.

The aldehyde functional group can be characterized by the C-H stretching frequency of the aldehyde group. The C-H frequency is fairly independent of the molecule due to the influence of the carbonyl oxygen. The aldehydic stretching mode is usually two bands in the region of 2900 - 2700 cm^{-1} with one near 2720 cm^{-1}. The C-H in-plane and out-of-plane deformations are less characteristic. The out-of-plane deformation falls in the region of 975 - 780 cm^{-1} and the in-plane deformation falls near 1400 cm^{-1}, but it is fairly weak and often masked by other absorptions in the region. There is no strong evidence of the C-H stretching absorption in the region of 2900 - 2700 cm^{-1}, however, there is a shoulder on the right side of the bands in the C-H region near 2700 cm^{-1} in two of the commercial shellac spectra. The band which is located in the region of 945 - 947 cm^{-1} in the sample spectra (and appears as a doublet in the spectrum of one of the commercial shellacs, NJS2) may be due to the C-H out-of-plane deformation. It may also be due to the out-of-plane O-H deformation in the carboxylic acid which falls in the range of 950 - 900 cm^{-1} (Bellamy, 1975) or a combination of both.

There are three broad bands in the spectra of the shellac samples which occur in the ranges of 1235 - 1253 cm^{-1}, 1162 - 1170 cm^{-1}, and 1030 - 1048 cm^{-1} which are thought to result from a combination of bands due to the C-O stretching vibrations in the carboxylic, hydroxyl and ester functional groups. The band in the range of 1235 - 1253 cm^{-1} is thought to be due to a combination of the C-O stretch and O-H deformation in a primary or secondary alcohol, the range of which is given by Bellamy (1975) as 1350 - 1260 cm^{-1} and the C-O stretch and O-H deformation in carboxylic acids which is listed as a strong absorbance at 1320 - 1211 cm^{-1} (Bellamy, 1975). The absorption in the region of 1147 - 1170 cm^{-1} probably results from the C-O stretch in the ester functional groups which is reported to fall in the range 1200 - 1100 cm^{-1} (Bellamy, 1975). There is a very weak absorption in the region of 1114 cm^{-1} in the shellac spectra which may be due to the second absorption of the O-H deformation and C-O stretch of a secondary alcohol which is expected to fall near 1100 cm^{-1} (Bellamy, 1975). The absorption in the region 1040 - 1048 cm^{-1} are thought to result from the second O-H deformation and C-O stretch which is expected to occur near 1050 cm^{-1} in primary alcohols.

The absorption in the region of 945 - 948 cm^{-1} may be due to either the O-H out-of-plane deformation in carboxylic acids or the C-H out-of-plane deformation in aldehydes which occur in the range of 950 - 900 cm^{-1} and 975 - 780 cm^{-1} respectively. It may also be a combination of both. The weak absorption which occurs in some of the spectra in the region of 772 - 799 cm^{-1} may be related to the aldehyde functional group instead. (The absorption which occurs at 772 cm^{-1} in one of the commercial shellac spectra (BM1) is of stronger relative intensity than in the other spectra.) The shellac spectra also exhibit an absorption in the region 723 - 725 cm^{-1} which results from the rocking vibrations of aliphatic chains of four or more methylene groups often observed in the region of 720 - 750 cm^{-1}. This is caused by the aliphatic acids which make up the lac resin molecule.

Identification of unknown sample

A schist relic box (2nd century B. C. - 2nd century A. D.) produced in the Gandhara region (present day Pakistan and Afganistan) was decorated with an incised design which was filled with a pale yellow paste. A small sample was removed for analysis. The sample was placed onto the silicon carbide paper

and crushed with the back of a microspatula. The resulting diffuse reflectance spectrum (Figure 7.8b) was observed to resemble the spectra of the shellac standards. The computerized search utilizing the SEARCH (peak) mode produced a list which included five of the reference spectra of shellac as the top five possible identifications. The first choice was commercial white shellac (Figure 7.8a). It is assumed that the commercial product was bleached in some way and perhaps contained a colouring agent of some type. However, the pale yellow colour of the unknown sample suggested that it had been processed in some way before use.

The characteristic frequencies of the diffuse reflectance spectrum of the unknown sample are listed in Table 7.6 with the ranges of the known samples. The frequencies fall within the ranges fairly consistently, but there are some differences in the C-O stretching region which may be due to ageing. The band which appears in the region of 1162 - 1170 cm^{-1} in the standard spectra occurs as two shoulders on the band at 1249 cm^{-1} which itself appears as a doublet in the sample spectrum. The band in the region of 1040 - 1048 cm^{-1} in the shellac reference spectra appears as a doublet near 1040 and 1019 cm^{-1} with the maximum

intensity at 1019 cm^{-1} in the sample spectrum. This absorption is also more intense in relation to the other absorptions in the spectrum of the unknown material than in the shellac spectra. Also, the band in the region of 945 -947 cm^{-1} in the reference spectra is not evident in the unknown sample spectrum where a shoulder appears on the band at 1019 cm^{-1}. Also, two weak bands occur near 760 and 780 cm^{-1} in the unknown sample spectrum. The changes in the spectrum are probably due to alterations in the structure due to cross-linking. It was thought that perhaps the differences may be due to the bleaching process, however, the sample of commercial bleached shellac, which is reported to have become insoluble in alcohol exhibits a spectrum which is very similar to the other shellacs in the region discussed above. The differences in the band assigned to the O-H deformation and C-O stretch in primary alcohols may be affected by the transition of these groups to esters in the cross-linking process. However, the corresponding ester C-O stretching absorption is less intense and occurs as a shoulder in the region of 1175 cm^{-1}. It may be that excessive cross-linking has resulted in a large polyester molecule with restricted vibrational movement.

Tar and pitch

Source

As mentioned above, tar is the distillate of the destructive distillation of hard or soft woods and pitch is the residue left from distillation (Forbes, 1936; Mills and White, 1987). Hard wood tars are obtained from broad leaf, deciduous trees such as maple, birch, beech, oak and ash and soft wood tars are produced from conifer trees such as pine, fir , cedar, spruce and larch. Pitch may also be prepared from tree resin (oleo-resin) by destructively distilling the rosin (Abraham, 1936). Pitch may be prepared by heating the tar to reduce the volatile components and thicken the substance. This produces a material which is more highly polymerized and known as pitch (Evershed et al., 1985).

The destructive distillation of wood was known in antiquity (Abraham, 1938). Pliny records a production method for softwood tar (Natural History, XVI, 52 - 53): "In Europe tar is obtained from the torch-pine by heating it, and is used for coating ships' tackle and many other purposes. The wood of the tree is chopped up and put into ovens and heated by means of a fire packed all round outside. The first liquid that exudes flows like water

down a pipe; in Syria this is called 'Cedar-juice' and it is so strong that in Egypt it is used for embalming the bodies of the dead. The liquor that follows is thicker and now produces pitch; this in turn is collected in copper cauldrons and thickened by means of vinegar, as making it coagulate, and it has been given the name of Bruttian pitch; it is only useful for casks and similar receptacles, and differs from other pitch by its viscosity and also by its reddish colour and because it is greasier than all the rest."

Pliny also mentions the production of pitch from resin (Natural History, XVI, 53): ".. caused to boil by means of red-hot stones in casks made of strong oak, or if casks are not available, by piling up a heap of billets, as in the process of making charcoal." He also wrote that this product was used for seasoning wine.

Composition

The chemical composition of wood and resin tars has not been extensively studied. However, it is thought that the structure would be similar for both materials as during the distillation process, the wood tar is created from the resin in the wood. The

major constituents of coniferous resin are abietane acids which will be discussed in a later section. Gas chromatography was utilized (Mills and White, 1987) to examine methylated samples of tar produced from softwood tar and tar made from rosin. The primary component of wood and resin tars was observed to be methyl dehydroabietate. Other components which were isolated in lesser amounts in both samples include retene, 1,2,3,4-tetrahydroretene, 18-nor and 19-norabietatriene. Methyl abietate was observed in the spectrum of the softwood pitch which is not strongly evident in that of the rosin pitch and both spectra contain a peak due to methyl 7-oxodehydroabietate. There is evidence of residual cellulose and lignin in the chromatogram of the tar produced from softwood (Mills and White, 1987).

In the study of the pitch from the Mary Rose (Evershed et al., 1985), the samples were analysed by gas chromatography/mass spectrometry. The samples were observed to contain methyl dehydroabietate, dehydroabietic acid, retene and minor amounts of other alkyl substituted tricyclic diterpenoid hydrocarbons. Stockholm tar prepared from wood from Pinus sylvestris was analysed in the same manner and the similarity in composition of the Mary Rose samples to that of the Stockholm tar strongly

supported pine wood as the starting material of the pitch samples from the Mary Rose. In these samples, no evidence of the underivatized abietic acid was found in the pitch samples or in the standard Stockholm tar. It was suggested that the derivatives of the resin acid are created by the destructive distillation which modifies the original resin acid by dehydrogenation and a certain amount of decarboxylation (Evershed et al., 1985). The methyl ester of abietic acid was found by Mills and White (1987) in the chromatogram of the softwood tar. It is possible that the degree of change is affected by the duration of the distillation process.

Tar and pitch may also be produced from coal. The material may be pyrolyzed to produce a tar as a distillate and a higher molecular weight pitchy material fuses and separates from the coke residue. Phenols, heterocyclics and polynuclear aromatic hydrocarbons are constituents of the tar. Coal tar was first prepared in the nineteenth century (Mills and White, 1987).

Interpretation of standard spectra

Spectra were obtained of softwood tar, pine rosin tar and softwood tar which had been aged for 11 years (Samples provided

by R. White, National Gallery). Samples which were labelled as wood tar pitch and wood or Stockholm tar (Institute of Archaeology Mineralogical collection) and a commercial specimen of Stockholm tar (British Museum Research Lab) were examined. Spectra were obtained of the fresh softwood tar, pine rosin tar and wood tar and further spectra were obtained after the liquid samples had been allowed to dry for two weeks and for nine months. In addition to the softwood tars, two samples of hardwood pitch or bistre from birch bark and beech wood were examined and one sample of aged coal tar (samples provided by R. White).

Ten spectra of the various softwood tars were obtained and the range of frequency values is given in Table 7.7. The values for the commercial Stockholm tar are listed separately. Figure 7.9 compares the spectrum of softwood pitch dried for nine months to one of softwood pitch aged for eleven years. The spectra exhibit bands in the regions of 2962 - 2958 cm^{-1}, 2935 - 2928 cm^{-1} and 2874 - 2867 cm^{-1} which correspond to the C-H stretching regions given by Bellamy, 2962 and 2872 ± 10 cm^{-1} for methyl groups and 2926 and 2853 ± 10 cm^{-1} for methylene groups. The band which is expected near 2872 cm^{-1} is masked and the band near 2962 cm^{-1} is

weaker and not always evident in the spectra. This indicates that there is a higher amount of methylene groups than methyl groups in the structure. An absorption is evident in the region 1464 - 1458 cm^{-1} and in the region 1384 - 1382 cm^{-1} which result from the deformations of the C-H linkages. The band near 1464 cm^{-1} is probably a combination of the asymmetrical stretch in the methyl group (1450 $\pm$ 20 cm^{-1}) and the deformation of the methylene group (1465 $\pm$ 20 cm^{-1}) and the second absorption is due to the symmetrical stretch of the methyl functional group (1380 - 1370 cm^{-1})(Bellamy, 1975).

There is evidence of aromatic groups in the spectra. There is a shoulder on the left side of the strong C-H stretching absorptions which is thought to be due to the aromatic C-H stretch. The regions given in the literature for this group are sharp, weak absorptions near 3030 and 3070 cm^{-1}. The weak bands appear as shoulders in these spectra. The absorptions are difficult to see when carboxylic acids are present as the O-H stretch appears as a shoulder on the C-H stretching absorptions. The tar spectra exhibit absorptions in the regions of 1607 - 1604 cm^{-1} and 1500 - 1498 cm^{-1} and sometimes a weak band is evident near 1646 cm^{-1} and 1515 cm^{-1}. These bands may be assigned to the

skeletal ring breathing vibrations. In the literature, two strong bands are observed in the regions 1625 - 1575 cm^{-1} and 1525 - 1475 cm^{-1} with two weaker bands, one near 1600 - 1560 cm^{-1} which often occur as a shoulder on the band near 1600 cm^{-1} and one near 1450 cm^{-1} which is often masked by the C-H bending vibrations. However, the range of the first band is extended to 1650 - 1585 cm^{-1} for some para-substituted and certain unsymmetrical tri-substituted compounds (Bellamy, 1975). Also in the case of fused ring systems, the band in the region 1600 - 1560 cm^{-1} is much more intense and appears as a distinct band (Bellamy, 1975).

The standard tar spectra exhibit a series of bands in the region of 900 - 700 cm^{-1} which may represent the C-H out-of-plane deformations in the aromatic ring. The band in the region of 888 - 886 cm^{-1} indicates the presence of rings with only one free hydrogen atom (900 - 860 cm^{-1}), the band in the area 825 - 819 cm^{-1} corresponds to rings with two adjacent free hydrogen atoms (860 - 800 cm^{-1}) and the band in the region of 758 - 755 cm^{-1} may be the result of either rings with four adjacent free hydrogen atoms (770 - 730 cm^{-1}) or five adjacent free hydrogen atoms (770 - 730 cm^{-1}). When five adjacent free hydrogen atoms are present,

the band is accompanied by a second band in the region of 710 - 690 cm^{-1} which corresponds to the band in the region of 718 - 703 cm^{-1} in the standard tar spectra. There is a considerable variation in intensity in this region between spectra and this may be explained by the differences in composition between the sample spectra.

The presence of dehydroabietic acid in the softwood tar (Evershed et al., 1985; Mills and White, 1987) should give rise to bands which are characteristic of the carboxylic acid functional group. The tar standard spectra exhibit a broad absorption in the O-H stretching region with a maximum intensity in the region 3400 - 3250 cm^{-1} which appears as a shoulder on the C-H stretching absorption. In some cases, there is an additional maximum in the region 3198 - 3157 cm^{-1}. This corresponds to the O-H stretching absorption in carboxylic acids. The region given in the literature for this absorption in solid and liquid samples is 3000 - 2500 cm^{-1} with a pattern that includes a broad absorption in the region of 3000 cm^{-1} with several weaker bands which are masked by the C-H stretching absorptions. A characteristic weak absorption which is not hidden has been observed to occur near 2650 cm^{-1}. The spectra of the tars

contain a weak absorption in the region 2660 - 2640 cm^{-1} which is indicative of a carboxylic acid. The range of values observed for the tar spectra is higher than expected for the major absorption. This may be due to hydrolysis of the materials which would cause a broadening of the band.

Carboxylic acids are characterized by a C=O stretching vibration and absorptions which result from C-O stretching and O-H deformations. The region given by Bellamy (1975) for aryl carboxylic acids is 1700 - 1680 cm^{-1}. The tar spectra exhibit a band in the region 1702 - 1695 cm^{-1} with a less intense shoulder in the region of 1727 - 1725 cm^{-1}. The stronger band is thought to be due to the carbonyl group within the carboxyl functional group. Carboxylic acids also exhibit vibrations which arise in the regions 1440 - 1395 cm^{-1} and 1320 - 1211 cm^{-1}. The former region contains two fairly weak absorptions near 1430 cm^{-1} and 1300 cm^{-1} which are conventionally assigned to the C-O stretch and the O-H in-plane deformation respectively, although the bands are thought to be due to a combination of both vibrations which cannot be specifically assigned (Bellamy, 1975). These bands are not evident in the spectra of the tars and may be masked by the vibrations which occur in the neighbouring regions. The second

band which occurs in the region 1320 - 1211 cm^{-1} is somewhat more intense and is thought to be due to C-O stretching vibration, but the assignment is somewhat tentative (Bellamy, 1975). A band occurs in the region of 1279 - 1254 cm^{-1} in the tar spectra which is fairly intense and may correspond to the band in the region 1320 - 1211 cm^{-1}. There are bands which occur in the region of 979 - 966 cm^{-1} and, in some cases, in the region 910 - 908 cm^{-1} in the spectra of the tar standards which may be related to the absorption in the area 950 - 900 cm^{-1} assigned to the O-H out-of-plane deformation.

The methyl dehydroabietate reported to occur in tar produced from pine (Evershed et al., 1985) should result in absorptions due to the ester group in the spectra. Esters produce two strong bands in the infrared spectrum which result from to the C=O and the C-O functional groups (Bellamy, 1975). The range given for the carbonyl stretch is 1730 - 1717 cm^{-1} for alpha, beta-unsaturated and aryl esters. The weak absorption which occurs in the region of 1727 - 1725 cm^{-1} and sometimes appears as a shoulder on the band arising from the carboxylic acid has been assigned to the ester carbonyl absorption. This indicates that the acid component is present in greater amounts in the tar standards.

The second absorption due to the C-O stretch is more difficult to assign even though it is a strong band. Absorptions which occur in the region 1300 - 1000 cm^{-1} may result from a variety of C-O vibrations from acids, alcohols, ethers and esters. The frequency of the band is strongly affected by the environment of the group and may be altered by changes in the groups. Also, it is thought that the C-O stretching vibration is affected by neighbouring atoms and is not due to a C-O stretching motion alone (Bellamy, 1975). The spectra of the tar standards exhibit a strong absorption in the region 1193 - 1176 cm^{-1} with two medium absorptions in the region of 1133 - 1128 cm^{-1} and 1041 - 1037 cm^{-1}. It is not possible to assign the bands exactly, but some esters have been found to display more than one absorption in this region. Also, the complexity of the material and changes which take place during heating might cause changes in the frequencies. Thus, one or more of the bands are probably due to the C-O stretch in the ester groups.

Identification of unknown samples

Seventeen samples of luting material were analysed. The samples were obtained from five different ships which were reused as revetements in the Thames valley area in Medieval times. The

samples consisted of animal hair coated with a black substance. The black material was extracted using ethanol or methanol and the solvent was removed by evaporation. A yellowish black residue was left after evaporation of the solvent and diffuse reflectance spectra were obtained of these samples. In certain samples, the residue was still sticky after the solvent was removed and the samples were mixed with KBr to obtain a satisfactory spectrum.

Thirteen of the sample spectra were found to resemble those of the softwood tar. These included JS1, JS2, JS5, JS6, JS12, JS15, JS23,JS24, JS25, JS35, JS41, JS42 and JS43. The details of the samples are listed at the end of the section. Figure 7.10 compares the spectrum of the softwood pitch which has been aged for 11 years with sample JS1 which was found to have the closest fit. The spectrum of fresh softwood pitch is shown with one of sample JS43 in Figure 7.11. The range of frequency values are listed in Table 7.7 along with those of the softwood tars. The ship samples exhibit absorptions in the regions 3409 - 3209 cm^{-1}, 3082 - 3049 cm^{-1}, 2934 - 2927 cm^{-1}, 2871 - 2856 cm^{-1}, 1608 - 1603 cm^{-1}, 1468 - 1452 cm^{-1}, 1383 - 1364 cm^{-1}, 1207 - 1171 cm^{-1}, 1075 - 1036 cm^{-1}, 889 - 874 cm^{-1}, 825 - 805 cm^{-1}, 757 - 752 cm^{-1} and

706 - 700 cm^{-1} which correspond to those observed in the spectra of the softwood tar standards. There is widening of the ranges in some cases, but these variations may reflect the degradation which is expected in archaeological samples. The samples were exposed to waterlogged conditions which may have resulted in other reactions.

The sample spectra also contain absorptions in the regions 3192 - 3181 cm^{-1}, 2960 - 2957 cm^{-1}, 1651 cm^{-1}, 1507 - 1500 cm^{-1}, 968 - 953 cm^{-1} and 926 - 925 cm^{-1} which occur as weak absorptions or do not appear in every sample spectrum. The band which is evident in the region of 1279 - 1254 cm^{-1} in the standard spectra only appears as a very slight shoulder on the band in the region of 1207 - 1171 cm^{-1} in all but two of the sample spectra. Also, the band in the region of 1133 - 1128 cm^{-1} in the standard spectra which is not present in all of the compounds appears in most of the sample spectra in the region of 1145 - 1140 cm^{-1} with a shoulder near 1100 cm^{-1}. In certain cases, the band near 1140 cm^{-1} is not evident, but a weak, but distinct band is evident in the region of 1128 - 1113 cm^{-1}. Both bands were evident together in only one sample spectrum. A band is apparent in the region of 1229 -1227 cm^{-1} in two of the sample spectra.

The major variation observed is in the absorption band in the carbonyl region. In the sample spectra, the carbonyl region has a maximum absorption in the range 1733 - 1696 cm^{-1} with a slight shoulder in the area of 1695 cm^{-1}. In the standard spectra, the maximum intensity is observed in the region 1702 - 1695 cm^{-1} with a weak band in the region 1727 - 1725 cm^{-1}. This phenomenon coupled with the loss of the band in the region of 1279 - 1254 cm^{-1} indicates that the carboxylic component in the sample has been severely decreased. This may be due to reactions which occur during degradation. A second explanation is that the carboxylic acids were ionized during burial forming salts and the treatment of the sample with acid before extraction was not sufficiently strong to convert the salts to the acid and subsequently the carboxylic acid was not extracted.

Four of the samples, JS3, JS7, JS14 and JS19, which were analysed did not result in spectra which compared well with those of the softwood tars. The frequencies were similar, but the relative intensities of the bands in the region of 1700 - 1600 cm^{-1} were different. A visual inspection of the spectra indicated that they were more similar to those of the bitumen standards. It is possible that the material was more of a pitch-like material

which had been heated for a longer period of time or had undergone more severe degradation.

Two samples, JS2 and JS22, were analysed by gas chromatography/mass spectrometry. JS2 was found to contain dehydroabietic acid and some evidence of 7-oxodehydroabietic acid. Traces of retene-like compounds and fats were also observed. JS22 was found to contain evidence of animal fats and dehydroabietic acid as major components and possible traces of retene-like compounds. This information indicates that the material was a pine resin and supports the theory that a softwood pitch was used for the luting.

Unknown sample information

The terms "luting" and "caulking" are sometimes confused, but luting is a "distinct technique for waterproofing the wooden hulls of clinker (or lapstrake) built boats" (Sanson, 1988). The samples were originally obtained from the Museum of London and formed the basis of an undergraduate research project in the Department of Human Environment, University College London Institute of Archaeology (Sanson, 1988). There were a total of 43 samples, but due to the amount of time needed for extraction

of the samples, the samples which might be representative of various repairs were chosen. They are summarized below.

JS1 HOR 86 F1230 S525 Site - Kingston Horsefair Date - Medieval

JS2 245 BR 269 204 Site - 245 Blackfriars Road Date - Medieval

JS3 ABB 86 21 10 Site - Falstaff House Date - Medieval

JS5 HOR 86 F1230 Scarf in S454 Site - Kingston Horsefair Date - Medieval

JS6 HOR 86 F1230 S451 Site - Kingston Horsefair Date - Medieval

JS12 ABB 86 21 9 Setwork Site - Falstaff House Date - Medieval

JS15 ABB 86 21 12 Frag A Site - Falstaff House Date - Medieval

JS23 HOR 86 F1230 from under tingle Frag C Site - Kingston Horsefair Date - Medieval

JS24 HOR 86 F1230 S524 Frag B under tingle Frag D Site - Kingston Horsefair Date - Medieval

JS25 HOR 86 F1230 S542 under tingle Site - Kingston Horsefair Date - Medieval

JS35 HOR 86 from lap on boat plank 1008 sub-sample 1008A Site - Kingston Horsefair Date - Medieval

JS41 CUS 73 1.18 Site - Custom House Date - probably med. 13th century.

JS42 TL 74 1136/1 1383 Site - Trig Lane Date - before 1330 - 1380

JS43 Blackfriars III Site - bed of river Thames near Blackfriars Date - 15th century

Summary of sites (Sanson, 1988)

Falstaff House - located in Abbot's Lane which is off Tooley Street, London, S.E.1. Several boat planks were reused as waterfront revetments in Medieval era. Planks had tarred hair luting between overlaps.

245 Blackfriars Road - located on the Southwark side of Blackfriars Bridge, London. The tarred hair luting was obtained from a portion of a clinker built boat which was reused as revetments in Medieval times.

Blackfriars III - Samples came from a 15th century wreck which was excavated within a cofferdam located in the bed of the Thames near Blackfriars. The luting was tarred hair.

Customs House - located between Lower Thames Street in the City of London and the Thames river. The site contained a flat boat bottom with the keel removed leaving two half-moon shapes which had been reused as a revetment. The luting was composed of tarred hair and the date of the boat is thought to be mid 13th century as the revetments were dated to the late 13th or early 14th century.

Trig Lane - located in City of London. Two small revetments were found to have been made from boat planks. The luting was composed of tarred hair. The boat would seem to have a date some time before 1330 - 1380 which was the date of material found behind the revetments.

The luting from the clinker-built boats excavated from New Fresh Wharf, Lower Thames Street, London was composed of moss. No samples were analysed in this study.

Gums and gum resins

Gums

Source

Certain plants produce an exudate which is either soluble in water or a dispersible in water. These materials are high molecular weight polysaccharides (Mills and White, 1987). The materials which are referred to as hydrocolloids are viscous and gummy when obtained and become glassy masses when dried in air (Glicksman, 1996). The production mechanism is not understood. It is, however, thought to be related to a defence mechanism within the plant. For example, Acacia trees produce a greater quantity of exudate when grown in poor climatic conditions such as high elevation than when grown in optimum conditions. Acacia trees are often slashed to produce the gum (Glicksman, 1969). In some cases, plant seeds contain polymers composed of sugars other than glucose in addition to the starch (glucose polymers) reserves which serve as stored nutrition for growing plants. These materials have properties similar to those of the gums and may be utilized for similar purposes (Glicksman, 1969).

The materials which are of interest in this study are materials which are known or thought to have been exploited in antiquity.

The most important material is gum arabic which is the exudate from Acacia species. It was utilized in Ancient Egypt (Mills White, 1987) and is also referred to as gum acacia, Turkey gum and gum Senegal (Glicksman, 1969). Gum arabic is utilized today in applications such as the food industry and the primary source of the material is the Sudan. However, species of the Acacia are also found in India, Australia, Central America and southwestern North America in addition to Africa (Mills and White, 1987; Glicksman, 1969).

Gum tragacanth was known at least several centuries before Christ when it was mentioned by Theophrastus. The botanical sources for the material are varieties of the Astragalus genus of the family Leguminosae. Other terms for the material include bassora gum, hog gum, goat's thorn, leaf gum and Syrian gum. The material is collected from shrubs located in Asia Minor and in Iran, Syria and Turkey in the mountainous arid regions. The gum is produced by wounding the bark of the plant and collecting the exudate (Glicksman, 1969).

The occurrence of gum karaya is limited to India where there is widespread use of this exudate of the species Sterculia urens.

The material is also referred to as gum kadaya, Indian tragacanth, India gum and Sterculia gum. It is obtained by tapping the trees and collecting the lumps of exudate after it has hardened (Glicksman, 1969).

The only seed gum which is of interest is the material known as locust bean gum. The material is obtained from the fruit of the Ceratonia siliqua L. which is known as the locust or carob tree. The plant is the only species of the Ceratonia genus which is a member of the Leguminosae family. The long pod-shaped fruit contain seeds from which the gum is obtained. The tree originated in the Near East and Mediterranean, but it was introduced to Greece and Italy by the Greeks who transported it from Syria. Utilizing their trade routes, the Arabs brought the plant to Spain and Northern Africa. The material is known by various local names which include St. John's bread (Johannisbrot), gum gatto, gum hevo, janda gum, lakol gum, rubigum, lupogum, luposol, gum tragon, tragasol, tragarab, honey locust and algaroba. Ancient sources indicate that the material was used as food for both animals and humans and perhaps the most important known archaeological use is in ancient Egypt. The

material was incorporated as a paste used for mummy wrappings (Glicksman, 1969).

Composition

Gum arabic is a polysaccharide with a molecular weight which ranges from 250,000 to 1,000,000. The material is heterogeneous and it is thought that several different molecular compounds are present. It is thought to occur as a slightly acidic or neutral salt of a polysaccharide and calcium, magnesium and potassium ions are thought to be present. The principal structure has been described as a chain of beta-galactopyranose rings linked at positions 1 and 3 with side chains of galactopyranose units. The terminal groups are described as glucuronic acid or 4-O-methylglucuronic acid. The galactose side-groups are also substituted in the C-3 location by glucuronic acid and 4-O-methylglucuronic acid. The sugars D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid are detected after the hydrolysis of gum arabic. The proportions of the four compounds are different for different Acacia species, but all are present (Glicksman, 1969).

The precise chemical structure of gum tragacanth has not been elucidated. The approximate molecular weight is 840,000. The substance is thought to be a mixture of polysaccharides and the sugars which have been found to be present include D-galacturonic acid, D-galactose, L-fructose, D-xylose and L-arabinose. As with gum arabic, the acids are thought to exist as calcium, magnesium and potassium salts (Glicksman, 1969). Gum tragacanth is characterized by a water soluble portion which is called tragacanthin and a portion which swells which is known as bassorin. The tragacanthin is a relatively minor component with the bassorin constituting 60 -70%. The tragacanthin structure is described as ring of three molecules of glucuronic acid and one molecule of arabinose. Two arabinose structures are also present as a side chain. The bassorin is thought to be made of polymethoxylated acids with a complex structure. A minor amount of cellulose, starch and protein are reported to occur in gum tragacanth (Glicksman, 1969).

Gum karaya is also a complex polysaccharide. The molecular weight is very large, approximately 9,500,000. The material is partially acetylated and L-rhamnose, D-galactose and D-

galacturonic acid in a ratio of 4: 6: 5 have been detected after acid hydrolysis of the gum (Glicksman, 1969).

The seed gum, locust bean gum, has been observed to have a molecular weight in the region of 310,000. The structure has been reported to be a straight chain polymer of D-mannose units which form linkages at the C-1 and C-4 positions. The structure is characterized by a single side group of D-galactose on position C-6 on every fourth or fifth mannose ring, and is illustrated in Figure 7.12. Differences in the growth stage of the plant at the time of collection and other variations in plant locations are thought to explain the variations in relative amounts of D-galactose and D-mannose which have been reported. Locust bean gum may also contain small amounts of cellulose, protein, ash, and pentosan (Glicksman, 1969).

Identification and interpretation of standard spectra

Polysaccharides or sugars may be characterized by the furfural reaction in which the unknown material is treated with acid which produces furfural compounds by dehydration. These compounds produce Schiff bases when combined with aromatic amines such as aniline. The Schiff bases are marked by characteristic colours.

The classical method of analysis for polysaccharide materials is to hydrolyze the material using acid and then measure the sugar and uronic acid products. The materials may be separated by various types of chromatography. The sugars must be converted into derivatives before gas chromatographic analysis (Mills and White, 1987).

The infrared spectra of gums are very similar in the high frequency region. This is expected as the substances contain the same functional groups (Glicksman, 1969). It has been suggested that an infrared spectrum may be used to identify gums as a class of materials. For example, the spectrum of a polysaccharide is different from that of a protein which is soluble in water (Mills and White, 1987). Previous infrared analysis of polysaccharides (Birstein, 1975) were obtained using rather large amounts of sample and were described as uninformative (Mills and White, 1987). Also, water extraction which was used to purify the sample might contain water soluble salts which would distort the spectrum. This effect may be eliminated by treating the sample with methanolic hydrochloric acid (Mills and White, 1987). However, this problem is not encountered in this study which utilizes solid sample analysis.

The region near 1667 cm^{-1} is reported to be affected by techniques used to purify the materials and is thus not useful for identification (Glicksman, 1969). The archaeological samples are unlikely to have been treated by processes used in modern day purification methods. However, it is not certain what treatment may have been used with the samples used as standards.

The region 1429 - 667 cm^{-1} is thought to be characteristic for gums and correlations and variations in this region were used to divide the materials into groups. The materials designated as group I include locust bean gum while group II includes gum karaya and group III contains both gum arabic and gum tragacanth (Glicksman, 1969).

The gum diffuse reflectance spectra obtained for this thesis are characterized by broad bands. The bands which are common to all four spectra include a broad, rounded band with maximum intensity in the region 3436 - 3290 cm^{-1} which is representative of the many hydroxyl groups in the polysaccharide structures. An indistinct band occurs in the region 2939 - 2923 cm^{-1} which is the result of C-H stretching vibrations and is less intense in relation to the O-H absorption. The spectra are also marked by a

weak absorption in the region 2161 - 2140 cm^{-1}. This band is not evident in the spectra which have been published by Glicksman (1969) and may be a result of the differences in spectra acquisition such as sample handling. The spectra exhibit a stong absorption in the region 1651 - 1607 cm^{-1}, but a wide variation is observed in the location of the maximum intensity. A broad band is observed in the region of 1250 - 1000 cm^{-1}, but there are variations in the shape and the location of the maximum intensity which occurs in the range 1251 - 1227 cm^{-1} and 1150 - 1117 cm^{-1}. The region is most similar in the spectra of gum tragacanth and locust bean gum. All of the spectra are marked by a broad indistinct envelope which reaches from about 800 - 400 cm^{-1}, and is due to the overlap of many absorptions in the region. The frequency values and band assignments which have appeared in the literature (Birstein, 1975) are compared with those of the spectra obtained in this thesis in Table 7.8.

The spectrum of locust bean gum is marked by bands in the regions 866 and 810 cm^{-1} with a "trough" in between (Glicksman, 1969). This pattern is evident in the diffuse reflectance spectrum obtained in this study where bands are evident in the regions of

876 and 815 cm^{-1}. A valley is present in the region centred near 850 cm^{-1}.

The gum karaya spectrum is reported to contain intense absorptions near 1724 and 1250 cm^{-1} (Glicksman, 1969) which are evident at 1725 and 1251 cm^{-1} in the diffuse reflectance spectrum of the material obtained in this study. The bands may be the result of the acetyl groups which are thought to be included in the structure of the material. Acetate esters are reported to exhibit a C-O stretching absorption in the region 1250 - 1230 cm^{-1}, but the frequency 1725 cm^{-1} is slightly below the range for normal saturated esters, 1750 - 1730 cm^{-1} (Bellamy, 1975). The location of the band may be affected by differences in the molecular structure. The spectrum is also said not to contain a band at 1333 cm^{-1} (Glicksman, 1969). This is true for the diffuse reflectance spectrum of gum karaya, but it is not characteristic as the band is not evident in the spectrum of gum arabic and appears at 1315 cm^{-1} in the locust bean gum spectrum. There are differences reported in the relative intensities in the area 1176 - 833 cm^{-1} (GLicksman, 1969) and this region corresponds in part to the variation observed in the region 1250 - 1000 cm^{-1} which has been discussed. Variations are also said

to occur in the region between 833 - 667 cm^{-1}. In the spectrum of gum karaya which was reproduced (Glicksman, 1969), the region is very weak. In the spectra of gum arabic and gum tragacanth, there are minor bands evident. The detail is very hard to see and no precise bands were reported (Glicksman, 1969). However, the corresponding region in the diffuse reflectance spectra in this study are not very useful.

The spectra of gum arabic and gum tragacanth are said to correspond closely in the region 1176 - 909 cm^{-1} (Glicksman, 1969). In the diffuse reflectance spectra, however, the gum tragacanth spectrum is marked by a band with a maximum intensity at 1117 cm^{-1} and a second absorption at 1055 cm^{-1} with a broad shoulder which ends near 980 cm^{-1}. The band has a different shape in the gum arabic spectrum with distinct absorptions located near 1050 cm^{-1} and at 984 cm^{-1}. Also, there are variations between the materials in the regions 1429 - 1250 cm^{-1} and 909 - 526 cm^{-1} (Glicksman, 1969). The diffuse reflectance spectrum of gum tragacanth exhibits bands at 1372 and 1332 cm^{-1} which are absent in that of gum arabic. However, the region 909 - 526 cm^{-1} is not very informative. The gum tragacanth spectrum obtained in this study is characterized by a strong absorption at

1744 cm^{-1} which indicates a possible ester linkage in the structure. The doublet observed at 1744 and 1637 cm^{-1} in this study is visible in that reported by Glicksman (1969), but the feature is not mentioned, nor are any frequencies given.

Gum resins

Source

Gum resins are materials which contain both a resin component and a gum or water soluble polysaccharide portion. The materials of interest in this group include the species of Commiphoria and Boswellia in the Burseraceae family which are better known as myrrh and frankincense respectively. These materials were exploited in antiquity as perfumes and medicines and the sources are located in the Middle East. Also, some species of the conifer Araucaria family have been found to produce gum resins (Mills and White, 1987).

Composition

The resin component of the Commiphoria and Boswellia materials has been found to consist of triterpenoids. However, the composition of the polysaccharide components has not been elucidated (Mills and White, 1987).

Interpretation of standard spectra

For this study, two samples were obtained of gum myrrh (MW1 and MW9) and one of frankincence (MW2). In addition, samples were obtained of a material labelled "gum dammar" (MW5) and gum olibanum (frankincense) (MW3). With the exception of one gum myrrh sample (MW9), the diffuse reflectance spectra were observed to be very similar in form to those of the resins. The frequencies of the four spectra are listed in Table 7.9. They may be compared with those of the resins which are listed in Table 7.3. In general, the spectra have bands which are characteristic of the carboxylic functional group, which include a broad band with maximum intensity in the region of 3420 - 3395 cm^{-1} which runs into the strong C-H stretching absorptions, a weak shoulder on the low frequency side of the C-H bands in the region of 2700 - 2500 cm^{-1}, and a strong absorption in the region 1714 - 1704 cm^{-1}. In addition to these bands, the bands which occur in the region 1459 - 1455 cm^{-1} and 1383 - 1381 cm^{-1} are of nearly equal intensity. The spectra are also marked by bands or shoulders in the regions 1246 - 1230 cm^{-1} (except gum dammar), 1150 - 1139 cm^{-1} and 1052 - 1032 cm^{-1}. The region 1300 - 400 cm^{-1}1 in the gum dammar spectrum is marked by fairly distinct

bands and a doublet is observed with maximum intensity at 1285 cm^{-1}.

The spectrum of the second sample of gum myrrh (MW9) was found to resemble those of the gums (Table 7.8). The spectrum is characterized by a strong, rounded band with maximum intensity at 3416, a relatively weak band at 2936 cm^{-1}, a weak absorption at 2160 cm^{-1}, a broad band centred at 1607 cm^{-1} and a broad absorption in the region in between 1200 - 1000 cm^{-1} with maximum intensity at 1086 cm^{-1}. Also, the region 800 - 400 cm^{-1} appears as a rounded envelope with maximum intensities occurring at 729 and 623 cm^{-1}. The spectrum is also marked by a wide, weak absorption at 912 cm^{-1} which may correspond to absorptions evident in the spectrum of gum tragacanth at 921 cm^{-1} and of locust bean gum at 876 cm^{-1}.

Identification of unknown samples

An example of characterization of an unknown by diffuse reflectance FT-IR is a sample of linen from the reverse of an Egyptian cartonnage (Shearer, 1987). The date of the object is uncertain and may range from 300 B. C. to 4th century A. D. (Ptolemaic to Roman period). A preliminary spectrum was obtained

by rubbing the linen against the silicon carbide paper and recording the spectrum from the powder. The sample was extracted in both deuterated chloroform and diethyl ether to eliminate possible interferences from the linen. The sample was insoluble in the diethyl ether, but an orange residue was left after the evaporation of the deuterated chloroform. The diffuse reflectance spectrum of this material was found to resemble those of the gums. It is difficult to precisely identify specific gums from the infrared spectra and the unknown spectrum did not match any of the spectra exactly. However, the closest fits were observed with the unknown spectrum and those of gum arabic and gum myrrh (MW9). The spectrum of the unknown has been published with the spectra of gum arabic and gum myrrh (Shearer, 1987). The unknown spectrum is marked by a strong, rounded band centred at 3363 cm^{-1}, a weaker band located at 2914 cm^{-1}, a weak absorption at 2134 cm^{-1} and a broad absorption between 1200 - 980 cm^{-1} which are characteristic of the gums. In this spectrum, the maximum intensity of the band between 1200 - 980 cm^{-1} is 1110 cm^{-1} and a second, less intense maximum occurs at 1044 cm^{-1} which varies slightly from the gum spectra. Also, the broad, intense band with maximum intensity at 1648 cm^{-1} is somewhat higher than

the frequencies observed for the standards. The only other variations are that the band at 1323 cm^{-1} in the unknown spectrum is not very strong in the gum arabic and gum myrrh spectra and that the three shoulders located near 1282, 1233 and 1203 cm^{-1} in the spectrum of the unknown differ slightly from the gum spectra where a single band is evident in the region 1251 - 1227 cm^{-1}. The band at 905 cm^{-1} in the unknown spectrum may correspond to that observed at 912 cm^{-1} in that of gum myrrh. Also, there is more detail in the region between 700 - 400 cm^{-1} in the unknown spectrum which may be a result of the solvent treatment. The variations in the sample spectrum from those of the reference material may be due to either degradation or the presence of small amounts of additives.

A sample of red colouring matter (MFA14) was taken from the body of a Ptah sokar osiris figure (Boston Museum of Fine Arts 03.1625). The sample was rubbed onto silicon carbide paper and the diffuse reflectance spectrum was obtained. It was observed to correspond closely to those of the gums and gum myrrh (MW9). The spectrum exhibits a rounded, strong band with maximum intensity at 3379 cm^{-1}, a band at 2932 cm^{-1}, a weak absorption at 2136 cm^{-1}, an intense band at 1606 cm^{-1} and a strong, broad band

located between 1200 and 950 cm^{-1} which has two maximum absorptions near 1150 and at 1064 cm^{-1}. Also, a weak band with maximum intensity is located at 904 cm^{-1} which may correspond to similar absorptions in the spectra of gum tragacanth, gum myrrh, locust bean gum and in unknown HK4. The region 700 - 400 cm^{-1} appears as a rounded hump with no strong absorptions. It is not possible to make a certain identification, but the spectrum is most similar to those of the locust bean gum and gum arabic in the region between 1500 and 900 cm^{-1}. The sample spectrum (Figure 7.14a) may be compared to those of locust bean gum and gaum arabic (Figure 7.13). It is possible that the gum material was utilized as a medium for the colouring matter.

A sample of black, brittle resin (MFA16) from the Anubis figure on the outermost coffin of Nesmutaatneru (Boston Museum of Fine Arts 95.1407) was examined. The sample was rubbed onto silicon carbide paper and the diffuse reflectance spectrum was measured from the paper. The resulting spectrum (Figure 7.14b) was found to exhibit bands which are considered characteristic of the gums. In addition to the bands located at 3354, 2923, 2135 and 1607 cm-1 and a broad absorption with maximum absorption at 1138 and 1050 cm^{-1} which correspond to spectra which have been discussed, the

spectrum contains a band at 1713 cm^{-1}. This feature is evident in the spectra of gum tragacanth and gum karaya, however, the frequency of the band in the former spectrum is much higher (1744 cm^{-1}) and the geographical provenance would indicate that the latter material is an unlikely match. It is more likely that the sample contains a minor component which has a carbonyl group. The remaining regions of the unknown spectrum are similar to those of the gum resins with a weak band centred at 883 cm^{-1} and a broad, indistinct region from 700 to 400 cm^{-1}. The region between 1500 and 900 cm^{-1} in the unknown spectrum (Figure 7.14b) is most similar to the corresponding region in those of gum arabic and locust bean gum (Figure 7.13).

A sample (NJS12) was obtained from the residue inside a gold relic box (Institute of Archaeology laboratory number 3900) from the Gandhara region, which is present day Pakistan and Afganistan. The material was examined by diffuse reflectance and the resulting spectrum was found to correspond closely to those of the gums. The unknown sample spectrum exhibits bands at 3299 cm^{-1} (rounded, broad), 2930, 2141 and 1629 cm^{-1}. The spectrum also contains a weak band at 932 cm^{-1} and a broad area of absorption from 700 to 400 cm^{-1}. The region of intense

absorption between 1200 and 980 cm^{-1} is marked by three fairly distinct bands at 1153, 1080 and 1030 cm^{-1} and the shape of the band is somewhat different from those of the standard gum spectra. Also, the region between 1500 - 1200 cm^{-1} is marked by a series of weak absorptions which also differs from the corresponding regions in the gum spectra. The region 1500 - and 1200 cm^{-1} in the unknown spectrum is most similar to the corresponding regions in the gum arabic and gum myrrh (MW9) spectra. The sample was identified as myrrh by gas chromatography/mass spectroscopy (Raymond White, personal communication). The spectrum of the unknown is compared to that of gum myrrh in Shearer, 1988 .

Figure 7.1 Structure of isoprene (Mills and White, 1987).

Figure 7.2 Structures of some abietane and pimarane diterpenoid components of conifer resins (Mills and White, 1987).

Figure 7.3 Structures of some labdane diterpenoid components of conifer resins (Mills and White, 1987).

Figure 7.4 Structures of the dammarane (I), euphane (II), ursane (III) and oleanane (IV) skeletons (Mills and White, 1977).

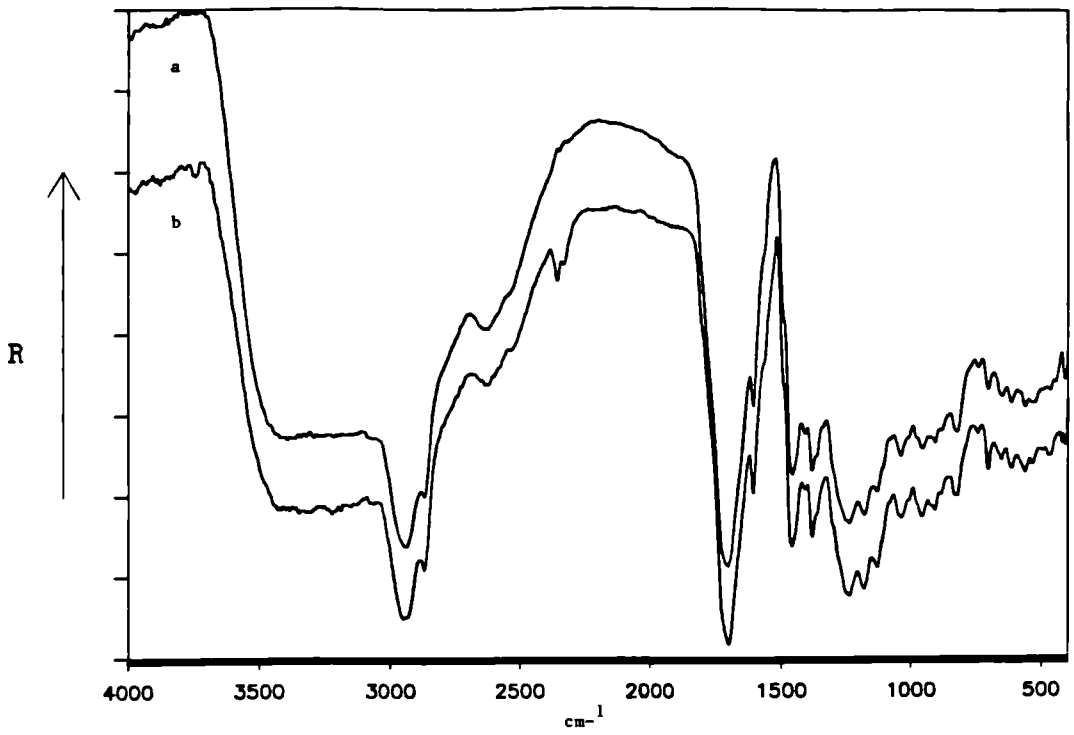

Figure 7.5 Diffuse reflectance spectra of (a) resin from Pinus massoniana (Kew10 Museum of Economic Botany, Kew) (gsva0070) and (b) material from reverse of Chinese bronze mirror (RK4 Victoria and Albert Museum FE87 1982) (gsva0349).

Image removed due to third party copyright

Figure 7.6 Structures of lac acids: jalaric acid (I), aleuritic acid (II), epishelloic acid (III), epilaksholic (IV), shelloic acid (V) and laksholic acid (VI) (Singh et al., 1974b).

Figure 7.7 Proposed structure of "pure lac resin" (Singh et al., 1974b).

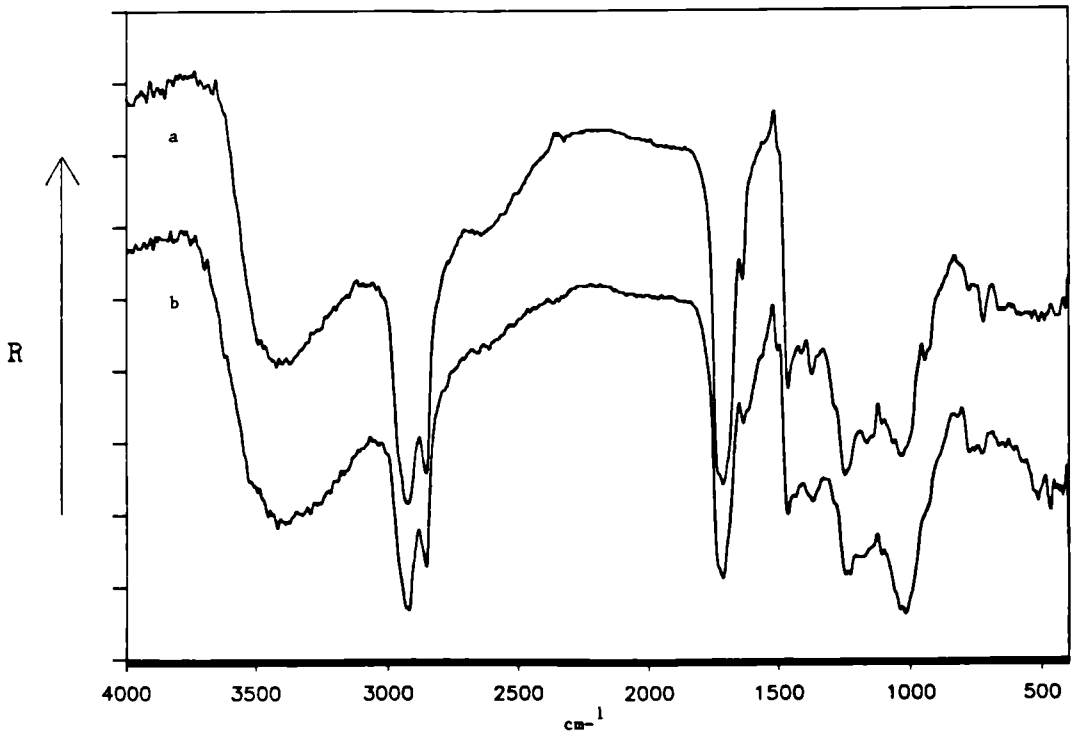

Figure 7.8 Diffuse reflectance FT-IR spectra of (a) commercial white shellac (VA4) (gsva0223) and (b) inlay paste from schist relic box from the Gandhara region (NJS7) (gsva0209).

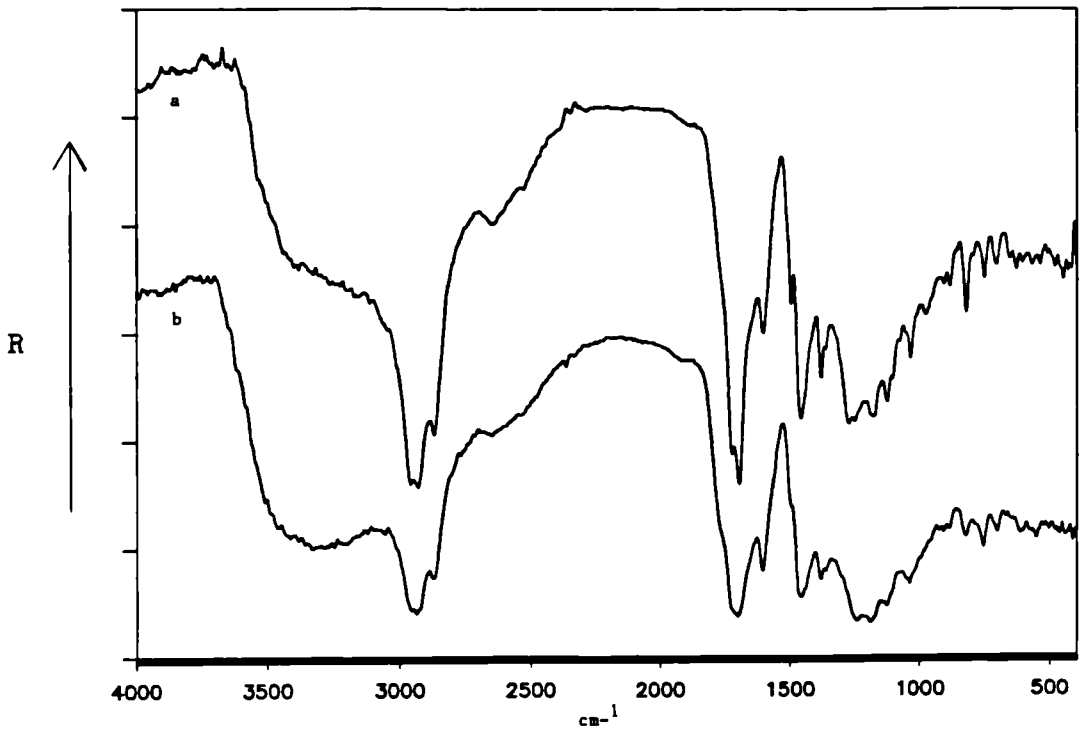

Figure 7.9 Diffuse reflectance FT-IR spectra of (a) softwood pitch (Pix liquida) dried for nine months (RW1) (gsva0387) and (b) softwood pitch (pix liquida) aged for eleven years (RW9) (gsva0228).

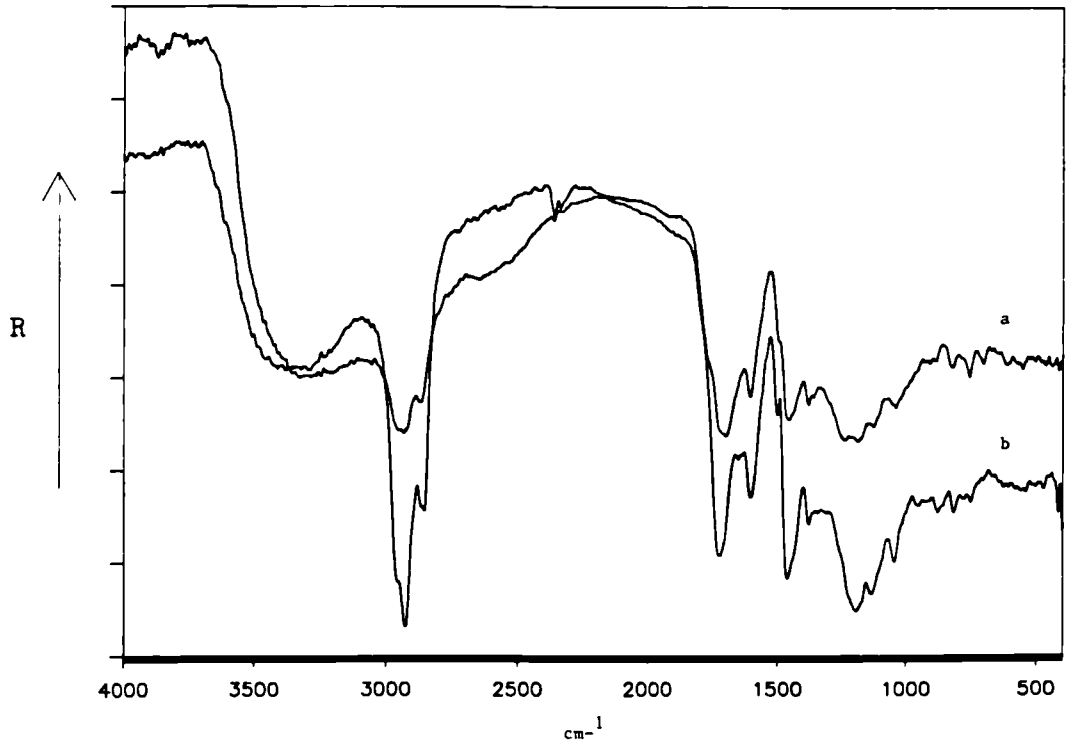

Figure 7.10 Diffuse reflectance FT-IR spectra of (a) softwood pitch (see Figure 7.9b) and (b) sample from ship luting (JS1 HOR 86 F1230 S525) (gsva0374).

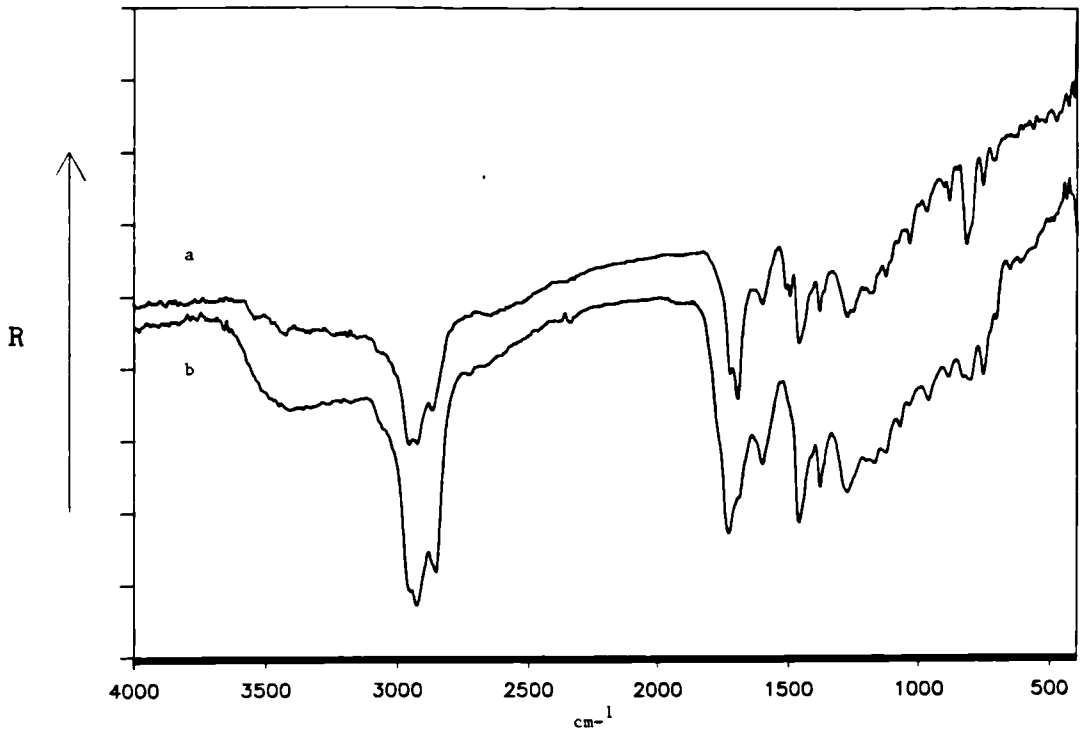

Figure 7.11 Diffuse reflectance FT-IR spectra obtained using KBr powder with silicon carbide paper of (a) fresh softwood pitch (Pix liquida) (RW1) (gsva0615) and (b) sample from ship luting (JS43 Blackfriars III) (gsva0562).

Figure 7.12 Structure of locust bean gum (Glicksman, 1969).

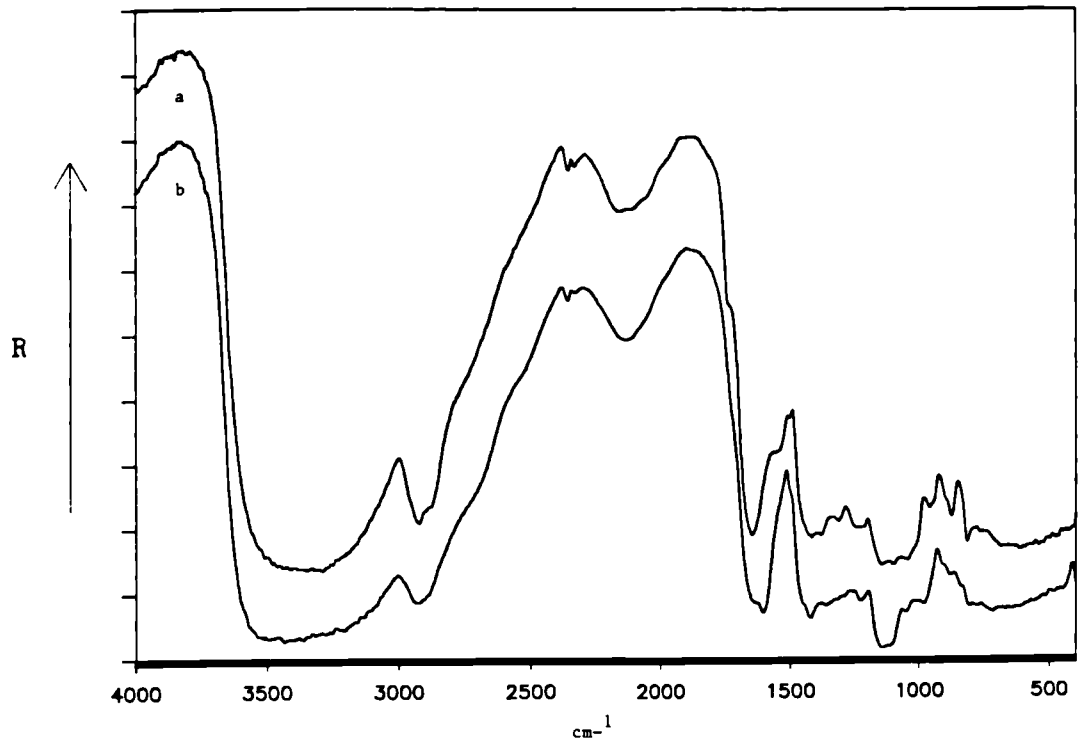

Figure 7.13 Diffuse reflectance FT-IR spectra of (a) locust bean gum (MW6) (gsva0028) and (b) gum arabic (MW8) (gsva0030).

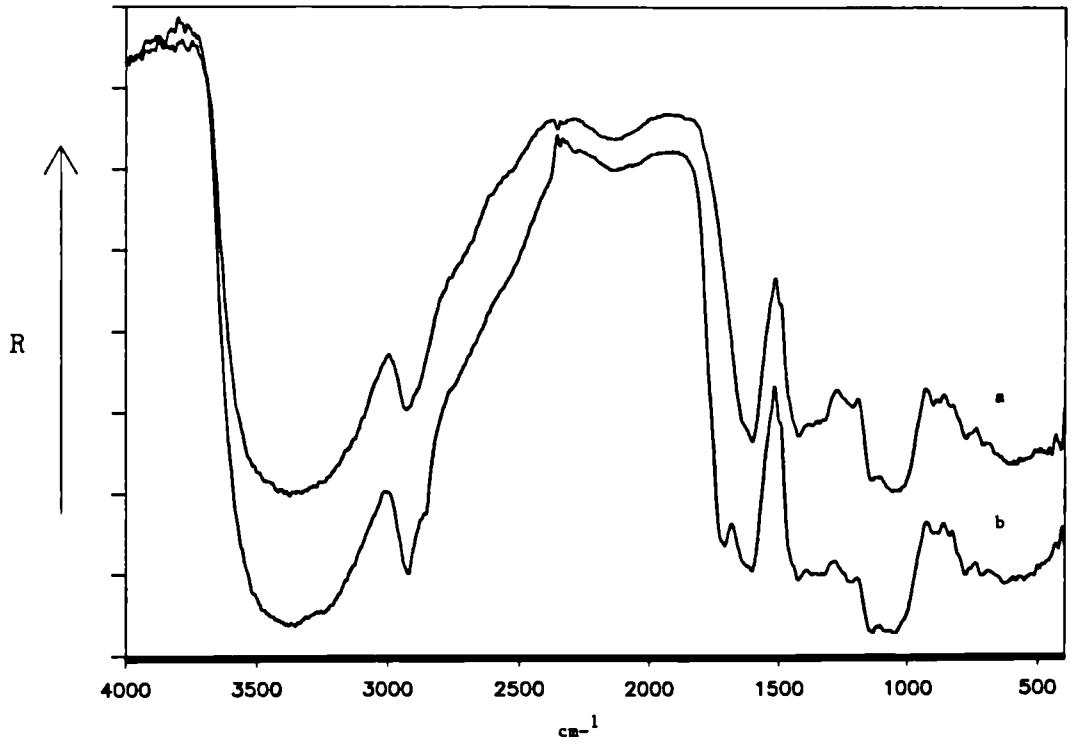

Figure 7.14 Diffuse reflectance FT-IR spectra of (a) red colouring matter from Ptah sokar osiris figure (mfa14 Boston Museum of Fine Arts 03.1625) (MFA14) and (b) black material from Anubis figure on the outermost coffin of Nesmutaatneru (mfa16 Boston Museum of Fine Arts 95.1407) (MFA16).

TABLE 7.1

Diterpenoid natural resins and their sources (Mills and White, 1987)

Coniferae			Leguminosae
Pinaceae	Cupressaceae	Araucariaceae	
Pinus species (Common or Bordeaux turpentine, rosin or colophony)	Tetraclinis articulata (sandarac)	Agathis species (kauri, manila)	Hymenaea species (East African or Zanzibar copal; Brazil copal)
Picea species (Burgundy pitch; scrape resin)	Juniperus species	Araucaria species	Copaifera species (copaibas)
Abies species (Strasbourg turpentine; Canada balsam)	Cupressus species		Guibourtia; Tessmannia; Daniellia; (other African copals; Congo, Accra, Benguela, Sierra Leone, etc.)
Larix species, notably L. decidua (Venice turpentine) Pseudotsuga menziessii (Oregon balsam)			

TABLE 7.2

Di- and triterpenoid resins obtained for this study from Kew

Diterpenoids									
Coniferae								Leguminosae	
Pinaceae			Cupressaceae		Araucariaceae				
Pinus kesiya	Kew9		Tetraclinis articulata	Kew17	Agathis australis	Kew1		Hymenaea verrucosa	Kew18
Pinus massoniana	Kew10				Agathis dammara	Kew2		Hymenaea courbaril	Kew19
Pinus merkusii	Kew11				Agathis dammara	Kew3			
Pinus roxburghii	Kew12		Juniperus phoenicea	Kew16					
Pinus sylvestris	Kew13				Araucaria columnaris	Kew4			
Pinus palustris	Kew25								
			Callitris gndlicheg	Kew14					
Picea abies	Kew7		Callitris verrucosa	Kew15					
Picea glauca	Kew8								
Abies spectabilis	Kew5								
Cedrus brevifolia	Kew6								
	Kew28								
Triterpenoids									
Anacardiaceae									
Pistacia lentiscus	Kew20								
Pistacia lentiscus	Kew21								
Pistacia terebinthus	Kew22								

TABLE 7.3

Frequency ranges and band assignments for resin standards (natural surfaces)

Coniferales			Leguminosae	Anacardiaceae	Assignment		
Araucariaceae	Pinaceae	Cupressaceae	Hymenea	Pistacia	Vibration		Frequency range given in literature (1)
cm-1	cm-1	cm-1	cm-1	cm-1			cm-1
3454 - 3250(sh)	3467 - 3164(sh)	3419 - 3188(sh)	3413 - 3375(sh)	3442 - 3419(sh)	O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)
					O-H stretch	O-H group intermolecular bonded	3400 - 3200(b,vs)
3079 - 3076(w)	3075 - 3066(w)	3079 - 3077(w)	3080 - 3079(w)		C-H stretch	C=C bond	3095 - 3075(m) 3040 - 3010(m)
2954 - 2917(s)	2942 - 2932(s)	2939 - 2925	2940 - 2938(s)	2957 - 2953(s)	C-H stretch	methyl group	2962 ± 10(s)
						methylene group	2926 ± 10(s)
2873 - 2872(s)	2875 - 2871(s)		2873 - 2871(s)		C-H stretch	methyl group	2872 ± 10(s)
near 2850(s)						methylene group	2853 ± 10(s)
near 2680(w)	2650 - 2639(w)	2676 - 2672(w)	near 2659(w)		O-H stretch hydrogen bonded	carboxylic acid	near 2650(w)
1719 - 1698(s)	1704 - 1695(s)	1714 - 1697(s)	1715 - 1704(s)	1713 - 1712(s)	C=O stretch	carboxylic acid aryl	1700 - 1680(s)
					C=O stretch	carboxylic acid , unsaturated	1705 - 1690(s)
					C=O stretch	ketone	1725 - 1705
1645 - 1644	near 1643	near 1653	near 1645		C=C stretch	C=C bond non-conjugated	1680 - 1620(v)
	1611 - 1607				C=C stretch	C=C bond C-O or C=O conjugated	near 1600(v)
	1556 - 1496				unassigned		
1467 - 1450(1)	1462 - 1453	1455 - 1451	1452 - 1451	1462 - 1461	C-H asym. deform.	methyl group	1450 ± 20(m)
					C-H deformation	methylene group	1465 ± 20(m)

TABLE 7.3 contd.

Frequency ranges and band assignments for resin standards (natural surfaces)

Coniferales			Leguminosae	Anacardiaceae	Assignment		
Araucariaceae	Pinaceae	Cupressaceae	Hymenea	Pistacia	Vibration		Frequency range given in literature (1)
cm-1	cm-1	cm-1	cm-1	cm-1			cm-1
near 1413	1417 - 1402	1413 - 1412			C-O stretch/O-H deformation	carboxylic acid	1440 - 1375(w)
1385 - 1371	1388 - 1365	1385 - 1380	1387	1384 - 1383	C-H sym. deform.	methyl group	1380 - 1370(s)
near 1330					unassigned		
1315 - 1308		1316			C-O stretch/O-H deformation	carboxylic acid	near 1300(s)
1235 - 1223(s)	1278 - 1235(s)	1237 - 1236(s)	1241(s)		unassigned	carboxylic acid	1320 - 1211(s)
1183 - 1179(s)	1186 - 1176(s)	1181 - 1177(s)	1194 - 1176(s)	1191 - 1184	unassigned		
			1104		unassigned		
1047 - 1032	1049 - 1036	1051 - 1032	near 1043	1058 - 1040	unassigned		
964 - 961	960 - 950	960 - 950	near 949		O-H out-of-plane deformation	carboxylic acid	950 - 900(v)
751 - 750	747 - 743	752 - 750	747 - 746		unassigned		
713 - 702	715 - 705	703 - 699	near 701		C-H out-of-plane deformation	C=C bond (cis)	near 690

Unless otherwise indicated, the intensity of the bands are variable. Some absorptions are not present in all spectra.

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.4

Frequency ranges and band assignments for colophony and unknowns identified as resin or resin mixtures

Colophony BM16 cm-1	Resins cm-1	Resin mixtures cm-1	Vibration		Frequency range given in literature (1) cm-1
3396(sh)	3437 - 3181(sh)	3544 - 3229(sh)	O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)
			O-H stretch	O-H group intermolecular bonded	3400 - 3200(b,vs)
near 3060(w)	3084 - 3071(w)	3064 - 3031(w)	C-H stretch	C=C bond	3095 - 3075(m)
					3040 - 3010(m)
2937(s)	2970 - 2924(s)	2965 - 2923(s)	C-H stretch	methyl group	2962 ± 10(s)
				methylene group	2926 ± 10(s)
2872(s)	2876 - 2854(s)	2866 - 2853	C-H stretch	methyl group	2872 ± 10(s)
				methylene group	2853 ± 10(s)
2650(w)	2641 - 2627(w)	near 2650(vw sh)	O-H stretch hydrogen bonded	carboxylic acid	near 2650(w)
1703(s)	1726 - 1701(s)	1744 - 1706(s)	C=O stretch	carboxylic acid aryl	1700 - 1680(s)
			C=O stretch	carboxylic acid , unsaturated	1705 - 1690(s)
			C=O stretch	ketone	1725 - 1705
		1660 - 1652	C=C stretch	C=C bond non-conjugated	1680 - 1620(v)
	1610 - 1607	near 1609	C=C stretch	C=C bond C-O or C=O conjugated	near 1600(v)
1497	1499	1551 - 1507	unassigned		
1462	1463 - 1450	1463 - 1450	C-H asym. deform.	methyl group	1450 ± 20(m)
			C-H deformation	methylene group	1465 ± 20(m)

TABLE 7.4 contd.

Frequency ranges and band assignments for colophony and unknowns identified as resin or resin mixtures

Colophony BM16 cm-1	Resins cm-1	Resin mixtures cm-1	Vibration		Frequency range given in literature (1) cm-1
	1420 - 1416	near 1431	C-O stretch/O-H deformation	carboxylic acid	1440 - 1375(w)
1387	1387 - 1379	1386 - 1373	C-H sym. deform.	methyl group	1380 - 1370(s)
		1322 - 1319	C-O stretch/O-H deformation	carboxylic acid	near 1300(s)
1236(s)	1238 - 1223(s)		unassigned	carboxylic acid	1320 - 1211(s)
1184(s)	1215 - 1179(s)	1217 - 1174(s)	unassigned		
	1138 - 1132	1142 - 1125(s)	unassigned		
1041	1050 - 1039(b)	1076 - 1039	unassigned		
956	985 - 958	near 958	O-H out-of-plane deformation	carboxylic acid	950 - 900(v)
744	769 - 747	749 - 747	unassigned		
	730 - 728	728 - 698	C-H out-of-plane deformation	C=C bond (cis-)	near 690
709	708 - 695				

Unless otherwise indicated, the intensity of the bands are variable. Some absorptions are not present in every spectrum in range.

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.5

Frequency values and band assignments for amber samples

LA1 cm-1	LA2 cm-1	LA3 interior cm-1	LA3 crust cm-1	Lieto cm-1	High Down Hill interior cm-1	High Down Hill crust cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
3262(sh)	3406(sh)	3250(sh)	3262(sh)	3351(sh)	3426(sh)	3413(s,b)	O-H stretch	O-H groups free and bonded	3700 - 3100(b)	1
							O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)	2
	3078(w)	near 3070(w)	near 3070(w)	3090(w)	3089(w)		C-H stretch	C=C bond	3095(w)	1
2932(s)	2935(s)	2931(s)	2942(s)	2932(s)	2932(s)	2933(s)	C-H stretch	methyl group	2962 ± 10(sh)	1,2
							C-H stretch	methylene group	2926 ± 10(s)	1,2
near 2870(s)	2871(s)	2871(s)	near 2870(s)	2870(s)	2868(s)	2871(s)	C-H stretch	methyl group	2872 ± 10(sh)	1,2
							C-H stretch	methylene group	2853 ± 10(s)	1,2
********** (shoulder near 2700 - 2650) **********					2648(sh)	2600(sh)	O-H stretch hydrogen bonded	carboxylic acid	near 2650(w)	2
						2514(w)		calcium carbonate	2530(vw)	3
						1794(w)		calcium carbonate	1785(vw)	3
1735(s)	1723(s)	1736(s)	1733(s)	1714(s)	1724(s)	1704(s)	C=O stretch	esters and ketones	1770 - 1695(s)	1
							C=O stretch	carboxylic acid	1725 - 1700(s)	2
near 1650(sh)	near 1650(sh)	1646(w)	near 1650(sh)	near 1650(sh)	near 1650(sh)	1651(s)	O-H deformation	O-H group	1640	1
							C=C stretch	C=C bond	1680 - 1620(va)	2
1452(m)	1453(m)	1454(m)	1460(m)	1454(m)	1452(m)		C-H deformation	methylene group	1465 ± 20(m)	1,2
							C-H sym. deform.	methyl group	1450 ± 20(m)	1,2
						1451(vs)	calcium carbonate		1430(vs,b)	3
1381(m)	1382(m)	1377(m)	1383(m)	1382(m)	1381(m)	near 1380(sh)	C-H asym. deform.	methyl group	1380 - 1370(s)	1,2

TABLE 7.5 contd.

Frequency values and band assignments for amber samples

LA1	LA2	LA3 interior	LA3 crust	Lieto	High Down Hill interior	High Down Hill crust	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
********** (broad shoulder from 1260 - 1200 into band near 1165) **********						1250(vw sh)	C-O stretch	ester see text	1250 - 1175(sh)	1
1162(s)	1168(s)	1161(s)	1164(s)	1169(s)	1169(s)	1162(s)	C-O stretch	ester see text	1150(s)	1
1015(m)	1028(m)	1004(m)	1028(m)	1027(s)	1019(m)	1032(s)	C-H deformation	cyclohexane	1050 - 950(b)	1
			near 950(m,b)				unassigned			
890(m)	890(m)	889(m)	888(m)	near 890(w)	880(w)		C-H out-of-plane deformation	terminal olefin see text	885(va)	1
						876(sp)		calcium carbonate	877(s,sp)	3
near 860(w)	near 860(w)	near 859(w)	near 850(m)				unassigned			
			near 830(m)				unassigned			
			near 805(m)				unassigned			
	near 748(w)				748(w)		unassigned			
					710(w)	713(w)		calcium carbonate	715(w)	3

1. Beck et al., 1965
2. Bellamy, 1975
3. Miller and Wilkins, 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.6

Frequency values and band assignments for reference shellac specimens and unknown sample

Reference shellacs cm-1	Unknown cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
3421 - 3326(b)	3416(b)	O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)
		O-H stretch	alcohol	3400 - 3200(vs,b) polymeric intermolecular bonds
2933 - 2923(s)	2922(s)	C-H stretch	methylene group	2926 ± 10(s)
2858 - 2854(s)	2855(s)	C-H stretch	methylene group	2853 ± 10(s)
1717 - 1713(s)	1714(s)	C=O stretch	ester, aryl	1730 - 1717(s)
		C=O stretch	carboxylic acid aryl	1700 - 1680(s)
		C=O stretch	aldehyde, aryl	1715 - 1695
* 1641 - 1638(m)	1634(m)	unassigned		
1469 - 1464(m)	1466(m)	C-H asym. deformation	methyl group	1450 ± 20(m)
		C-H deformation	methylene group	1465 ± 20(m)
* 1418 - 1414(w)	1435(vw)	C-H in-plane deformation	aldehyde	near 1400(w)
1377 - 1375(m)	1371(m)	C-H sym. deformation	methylene group	1380 - 1370(s)
1253 - 1235(s)	1249(s)	C-O stretch/O-H deformation	alcohol primary or secondary	1350 - 1260(s)
		C-O stretch/O-H deformation	carboxylic acid	1320 - 1211(s)
1170 - 1147(s)	1193(sh)	C-O stretch	ester	1300 - 1000(s)
	1148(sh)	C-O stretch	ester	1300 - 1000(s)
* 1114(vw)	1113(w)	C-O stretch/O-H deformation	alcohol, secondary	near 1100(s)
1048 - 1030(s)	1019(s)	C-O stretch/O-H deformation	alcohol, primary	near 1050(s)
948 - 945(m)	937(sh)	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)
	885(sh)	unassigned		
* 799 - 772(w)	776(w)	C-H out-of-plane deformation	aldehyde	975 - 780(m)
	757(w)	unassigned		
* 725 - 723(m)	730(w)	chain rocking vibration	long chain hydrocarbons with four or more methylene units	750 - 720(m)
* 664 - 639(w)	641(w)	unassigned		
* 565 - 513(w)	515(w)	unassigned		

* Absorption is weak, occurs as a shoulder or is not apparent in some sample spectra

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.7

Frequency values and band assignments for tar standards and unknown ship luting samples

softwood tars cm-1	unknown ship samples cm-1	hardwood pitch cm-1	coal tar cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
3400 - 3250(sh,b)	3409 - 3209(sh,b)	3404 - 3325(m,b)	3284 - 3259(m,b)	O-H stretch	water	
*3198 - 3157(sh,b)	*3192 - 3181(sh,b)			O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)
near 3070(sh)	3082 - 3049(w)		3054 - 3052(m)	C-H stretch	aromatic ring	3070 and 3030(w)
2962 - 2958(sh)	* 2960 - 2957(sh)		2955(s)	C-H stretch	methyl group	2962 ± 10(s)
2935 - 2928(s)	2934 - 2927(s)	@ 2929 - 2927(m)	2928 - 2926(s)	C-H stretch	methylene group	2926 ± 10(s)
2874 - 2867(s)	2871 - 2856(s)	2856 - 2855(w)	2859 - 2858(s)	C-H stretch	methylene group	2872 ± 10(s)
				C-H stretch	methyl group	2853 ± 10(s)
2660 - 2640(w)				O-H stretch hydrogen bonded	carboxylic acid	near 2650(w)
			1922 - 1918(w)	unassigned		
1727 - 1725(sh)	1733 - 1696(s)			C=O stretch	ester , unsaturated	1730 - 1717(s)
				C=O stretch	ester, aryl	1730 - 1717(s)
1702 - 1695(s)	* near 1695(sh)	@ near 1700(sh)		C=O stretch	carboxylic acid aryl	1700 - 1680(s)
				C=O stretch	carboxylic acid , unsaturated	1705 - 1690(s)
* near 1646(sh)	* 1651(w)		1649(sh)	skeletal ring stretch	aromatic ring	1650 - 1585(s) unsym. tri-substitution
1607 - 1604(m)	1608 - 1603(s)	1610 - 1606(s)	1605 - 1603(s)	skeletal ring stretch	aromatic ring	1625 - 1575(va)
				skeletal ring stretch	aromatic ring	1600 - 1560(w unless conjugated)
* near 1515(sh)		@ 1513(m)		unassigned		
1500 - 1498(m)	* 1507 - 1500(w)		1501(sh)	skeletal ring stretch	aromatic ring	1525 - 1475(va)

TABLE 7.7 contd.

Frequency values and band assignments for tar standards and unknown ship luting samples

softwood tars cm-1	unknown ship samples cm-1	hardwood pitch cm-1	coal tar cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
1464 - 1458(s)	1468 - 1452(s)	1478 - 1465(s)	1461 - 1457(s)	C-H asym. deformation	methyl group	1450 ± 20(m)
				C-H deformation	methylene group	1465 ± 20(m)
1384 - 1382(s)	1383 - 1364(w)	@ 1333 - 1332(s)	1379 - 1378(s)	C-H sym. deformation	methyl group	1380 - 1370(s)
* 1279 - 1254(s)	** 1274 - 1267(s)			C-O stretch	carboxylic acid	1320 - 1211(s)
	***1229 - 1227(s)			C-O stretch	carboxylic acid	1320 - 1211(s)
1193 - 1176(s)	1207 - 1171(s)	1207 - 1193(s)	1205 - 1199(s)	C-O stretch	ester	1300 - 1100(s)
* 1133 - 1128(s)	* 1145 - 1113(s)	@ 1158 - 1150(s)		C-O stretch	ester	1300 - 1100(s)
1041 - 1037(s)	1075 - 1036(s)	1054 - 1043(s)	1038 - 1036(m)	C-O stretch	ester	1300 - 1100(s)
* 979 - 966(m)	* 968 - 953(va)	# 965(s)	956 - 952(m)	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)
* 910 - 908(va)	* 926 - 925(va)			O-H out-of-plane deformation	carboxylic acid	950 - 900(va)
888 - 886(va)	* 889 - 874(va)	@ 880(w)	869(sh)	C-H out-of-plane deformation	aromatic ring	900 - 860(m) one free H atom
825 - 819(va)	825 - 805(va)		816 - 815(s)	C-H out-of-plane deformation	aromatic ring	860 - 800(vs) para-substitution
758 - 755(va)	* 757 - 752(va)	@ 782 - 780(m)	754 - 752(s)	C-H out-of-plane deformation	aromatic ring	770 - 735(vs) ortho-substitution
				C-H out-of-plane deformation	aromatic ring	770 - 730(vs) mono-substitution
718 - 703(va)	* 706 - 700(va)	@ 697(m)		C-H out-of-plane deformation	aromatic ring	710 - 690(s) mono-substitution

* Absorption is weak or not apparent in some spectra.

** Absorption occurs in sample spectra of JH42 and JH43 only.

*** Absorption occurs in sample spectra of JH41 and JH42 only.

@ Absorption occurs in spectra of beechwood bistre only.

Absorption occurs in spectrum of birch bark bistre only.

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.8

Frequency values and band assignments for gum standards

MW8 cm-1	MW7 cm-1	MW4 cm-1	MW6 cm-1	MW9 cm-1	Vibration	Functional Group	Frequency value given in literature cm-1	Ref.
3436(s,b)	3405(s,b)	3397(s,b)	3290(s,b)	3416(s,b)	O-H stretch	O-H group hydrogen bonded	3400(s,b)	1
2923(m)	2938(m)	2939(m)	2924(m)	2936(m)	C-H stretch	methyl and methylene groups	3000 - 2800	1
2143(w,b)	2144(w,b)	2140(w,b)	2161(w,b)	2160(w,b)	unassigned			
	1744(m)	1725(m)			C=O stretch	carboxylic acid non-ionized	1740(w)	1
near 1650(sh)								
1607(m)	1637(m,b)	1608(m)	1651(m)	1607(m)	C=O stretch	carboxylic acid ionized	1640 - 1620(m)	1
						carboxylic acid ionized anti-symmetrical	1610 - 1550	2
1422(m)	1440(m)	1421(m)	1421(m)	1433(m)	C-H deformation	methyl and methylene groups	1500 - 1400(m)	1
					C=O stretch	carboxylic acid ionized symmetrical	1400 - 1300	2
	1372(w)	1375(w)		1378(w)	C-H sym. deformation	methyl group	1380 - 1370(s)	2

TABLE 7.8 contd.

Frequency values and band assignments for gum standards

MW8 cm-1	MW7 cm-1	MW4 cm-1	MW6 cm-1	MW9 cm-1	Vibration	Functional Group	Frequency value given in literature cm-1	Ref.
	1332(w)		1315(w)		unassigned			
1227(m)	1236(m)	1251(m)	1243(m)	1237(s)	unassigned			
1148(s,b)	near 1150(sh)	1148(s)	1149(s,b)		unassigned			
	1117(s,b)				unassigned			
near 1050(s,b)	1055(s,b)	1056(s,b)		1086(m)	inorganic components		1100 - 1000(s,b)	1
984(m)			960(m)		unassigned			
	921(m)	894(m)	876(m)	912(m)	unassigned			
near 810(w)		near 810(w)	815(m)	near 810(sh)	unassigned			
717(w)				729(w)	unassigned	broad area of absorption - see text		
	639(w)		614(w)	623(w)	unassigned			

1. Birstein, 1975
2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.9

Frequency values and band assignments for gum resin standards

MW1 cm-1	MW2 cm-1	MW3 cm-1	MW5 cm-1	Vibration	Functional group	Frequency values given in literature (1) cm-1
3420(m,b)	3397(m,b)	3395(m,b)	3414(m,b)	O-H stretch	O-H group intermolecular bonded	3400 - 3200(b)
				O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)
2953(s)	2950(s)	2953(s)	2953(s)	C-H stretch	methyl group	2962 ± 10(s)
2873(s)	2873(s)		2870(s)	C-H stretch	methyl group	2872 ± 10(s)
1704(s)	1714(s)	1704(s)	1706(s)	C=O stretch	carboxylic acid , unsaturated	1705 - 1690(s)
				C=O stretch	ketone	1725 - 1705
				C=O stretch	carboxylic acid aryl	1700 - 1680(s)
1672(m)	1663(m)	1662(m)	1645(m)	C=C stretch	C=C bond non-conjugated	1680 - 1620(v)
1508(w)				skeletal ring stretch	aromatic ring	1525 - 1475(v)
1455(m)	1459(m)	1455(m)	1459(m)	C-H asym. deform.	methyl group	1450 ± 20(m)
				C-H deformation	methylene group	1465 ± 20(m)
1382(m)	1382(m)	1381(m)	1383(m)	C-H sym. deform.	methyl group	1380 - 1370(s)
			1310(w)	C-O stretch/O-H deformation	carboxylic acid	near 1300
near 1230(sh)	1246(s)	1245(s)	1285(m)	C-O stretch or O-H deformation	carboxylic acid	1320 - 1211(s)
	1204(s)		1184(s)	unassigned		
near 1150(sh)	1140(s)	1139(s)	1147(s)	unassigned		
			1114(s)	unassigned		

TABLE 7.9 contd.

Frequency values and band assignments for gum resin standards

MW1 cm-1	MW2 cm-1	MW3 cm-1	MW5 cm-1	Vibration	Functional group	Frequency values given in literature (1) cm-1
			1082(m)	unassigned		
1044(b)	1032(b)	1052(b)	1046(b)	unassigned		
	993(w)		988(w)	unassigned		
			966(w)	unassigned		
near 920(w)			924(w)	O-H out-of-plane deformation	carboxylic acid	950 - 900(v)
			892(w)	unassigned		
	824(w)		832(w)	unassigned		
			812(w)	unassigned		
752(w)		777(w)	757(w)	unassigned		
	667(w)	665(w)	661(w)	unassigned		

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.10

Frequency values and band assignments for unknowns identified as gums

HK4 cm-1	MFA14 cm-1	MFA16 cm-1	NJS12 cm-1	Vibration	Functional Group	Frequency value given in literature cm-1	Ref.
3363(s,b)	3379(s,b)	3354(s,b)	3299(s,b)	O-H stretch	O-H group hydrogen bonded	3400(s,b)	1
2914(m)	2932(m)	2923(m)	2930(m)	C-H stretch	methyl and methylene groups	3000 - 2800	1
2134(w,b)	2136(w,b)	2135(w,b)	2141(w,b)	unassigned			
		1713(m)		C=O stretch	carboxylic acid non-ionized	1740(w)	1
1648(m,b)	1606(m,b)	1607(m)	1629(m)	C=O stretch	carboxylic acid ionized	1640 - 1620(m)	1
					carboxylic acid ionized anti-symmetrical	1610 - 1550	2
1429(m)	1430(m)	1430(m)	1459(m)	C-H deformation	methyl and methylene groups	1500 - 1400(m)	1
				C=O stretch	carboxylic acid ionized symmetrical	1400 - 1300	2
near 1371(sh)	near 1375(w)		1377(m)	C-H sym. deformation	methyl group	1380 - 1370(s)	2
1323(m)	near 1345(w)	1346(w)		unassigned			
near 1282(w)				unassigned			
near 1233(w)		near 1230(m)	1237(s)	unassigned			
near 1203(w)	1218(m)			unassigned			
	near 1150(s,b)	1138(s,b)	1153(s)	unassigned			
1110(s,b)	1064(s,b)	1050(s,b)	1080(s)	inorganic components		1100 - 1000(s,b)	1
1044(s)			1030(s)				

TABLE 7.10 contd.

Frequency values and band assignments for unknowns identified as gums

HK4	MFA14	MFA16	NJS12	Vibration	Functional Group	Frequency value given Ref. in literature
cm-1	cm-1	cm-1	cm-1			cm-1
905(m)	904(m)		932(m)	unassigned		
		883(m)	864(m)	unassigned		
		841(w)		unassigned		
	776(w)	780(w)	771(m)	unassigned		
614	(broad area of	absorption	700 - 400)	unassigned		

1. Birstein, 1975
2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

CHAPTER 8 PROTEINS

Source

Proteins are a class of compounds which occasionally may be encountered as or with archaeological objects. Proteinacious materials are susceptible to degradation processes and are not often found in archaeological contexts. However, some materials survive in special burial microenvironments. The most common example of an archaeological protein is leather. Also, proteins have been utilized as binding media and adhesives. Examples include animal glue, egg white (albumen), egg yolk (tempera) and casein (Kuhn, 1986). In addition, proteins are natural plastics and may be deformed under pressure. Materials such as horn and tortoiseshell have been moulded into objects which are beginning to appear in social history collections (see chapters 9 and 13 on plastics).

Structure and identification

Proteins are complex structures which are composed of amino acids linked together by peptide bonds (Figure 8.1). Proteins as a class of materials may be identified by the presence of certain bands in the infrared. The bands result from the peptide bonds which link the amino acid "building blocks" in the polymer chain.

The infrared spectra of proteins are fairly similar. A more sensitive technique such as gas chromatography is needed to make a more specific identification. Several methods of protein analysis are not feasible for art and archaeological specimens due to the large sample required (Mills and White, 1987).

Interpretation of standard spectra

Standard sample information

In this study, diffuse reflectance spectra were obtained of egg white, animal glue, rabbit skin glue, and hide glue in addition to three objects made of pressed horn and one object of tortoiseshell (Hawksbill turtle) (Chapter13). The frequency values and band assignments are listed in Table 8.1.

Interpretation of spectra

The characteristic protein spectrum is discussed in the casein section of chapter 10. In general, protein spectra are marked by several strong bands (Figure 8.2). The N-H groups are susceptible to hydrogen bonding within the polymer chain and with other polymer molecules. A strong, broad band is observed in the region of 3330 cm^{-1} and is thought to be characteristic of both the inter- and intramolecular hydrogen bonded N-H groups in the

protein structure. The spectra also contain two bands in the approximate areas 1650 and 1550 cm^{-1} which are referred to as the amide I and amide II bands respectively. The amide I band results from the C=O stretch and the amide II band is thought to be caused by a coupled C-N stretch and a N-H deformation. Differences in structure, such as change in conformation, may cause variations in frequency values. Protein spectra may also contain a weak absorption in the region of 3080 cm^{-1} which is thought to be an overtone of the amide II absorption. The other areas of the spectrum result from functional groups on the amino acid side chains (Bellamy, 1975).

The region near 1270 cm^{-1} is sometimes characteristic of secondary amides and is referred to as the amide III band. It may fall in the wide region of 1305 - 1200 cm^{-1} and is usually weaker in relation to the amide I or II bands. It is often blocked by other absorptions which occur in the region. The band is assigned to a coupled C-N stretch and N-H deformation (Bellamy, 1975). Absorptions in this region in a protein spectrum may be due to C-N or N-H vibrations.

The spectra of proteins are marked by a broad area of absorption in the region 800 - 400 cm^{-1}. This is probably the result of the overlap of many bands due to the complex structure of the proteins.

Identification of unknown sample

An archaeological specimen which was thought to be untanned skin (York2) was tentatively identified as a protein. Skin is composed of protein (33%) and water (65%) and will decay rapidly. However, skin may survive in a dry environment where it becomes brittle (Kuhn, 1986).

The band frequencies and band assignments are summarized in Table 8.1. The spectrum of the unknown sample is compared to that of tortoiseshell and pressed horn in Figure 8.2. The broad band with maximum intensity at 3308 cm^{-1} in the spectrum of the unknown is assigned to the bonded N-H stretching vibration. The unknown sample spectrum has bands at 1662, 1606 and 1422 cm^{-1} with a shoulder in the region of 1550 cm^{-1} on the band at 1606 cm^{-1}.

In addition to the amide bonds, the presence of bands near 1608 and 1400 cm^{-1} have been found in the spectra of dipeptides and

have been assigned to the COO^- group which is the ionized form of the peptide linkage. The band near 1600 cm^{-1} is assigned to the anti-symmetrical vibration and the absorption near 1400 cm^{-1} is assigned to the symmetrical vibration. The band near 1608 cm^{-1} often masks or partially obscures the amide II absorption and it is difficult to assign frequencies in this area. These band frequencies correspond well with the values given for the amide I band (1680 - 1630 cm^{-1}) and the ionized carboxyl group (1608 cm^{-1}). The shoulder near 1550 cm^{-1} is probably the partially obscured amide II band. The spectrum of the unknown material has an absorption at 1422 cm^{-1} which may relate to the band near 1400 cm^{-1} listed in the literature for the ionized carboxyl group. It would seem that the material is a protein which has undergone partial degradation (hydrolysis) which has resulted in the formation of ionized compounds.

In the unknown spectrum, a complex absorption with maximum intensities at 1270 and 1233 cm^{-1} is evident. It is possible that one or both of these bands are due to C-N stretching or N-H deformation vibrations. The weak absorption near 3080 cm^{-1} which has been tentatively identified as an overtone of the absorption in the region of 1550 cm^{-1} (amide II) is not particularly evident

in the unknown spectrum, but a weak shoulder may be seen on the right side of the N-H stretching absorption at 3308 cm^{-1} which may correspond to this absorption.

The other regions in the spectrum result from vibrations of the various amino acid groups. In complex proteins, a broad area of absorption is expected to occur in the region 800 - 400 cm^{-1}. This is not particularly evident in this unknown spectrum, but the presence of inorganic materials such as hair or dirt seems to cause loss of relative intensity which lowers the baseline severely in the region between 1600 - 400 cm^{-1} in the unknown sample spectrum.

The sample was identified on the basis of chemical information obtained from the frequencies as a partially degraded protein. This type of identification is usually aided by comparison with spectra of standard material of known identity. This is less useful with proteins as their infrared spectra tend to be very similar. Also, it is very difficult to recreate or estimate the reactions which take place during burial.

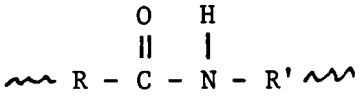

Figure 8.1 Structure of a peptide bond.

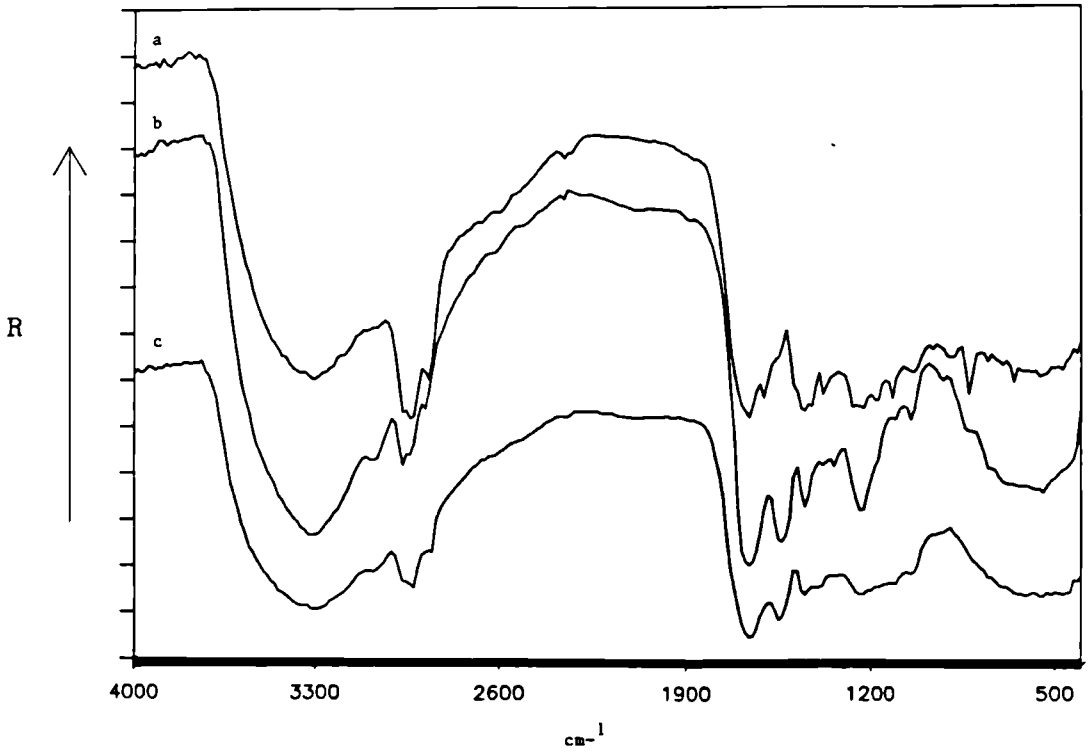

Figure 8.2 Diffuse reflectance FT-IR spectra of (a) unknown sample (York2) identified as a protein (York Archaeological Trust Conservation Laboratories) (gsva0573), (b) tortoiseshell hairbrush (PHS55) from Hawksbill turtle (Plastics Historical Society (phs0058) and (c) pressed horn seal (PHS25) (Plastics Historical Society) (phs0028).

TABLE 8.1

Frequency values and band assignments for proteinaceous materials

Albumen	Rabbit skin glue	Animal glue	Hide glue	Horn	Horn	Horn	Tortoise-shell	Unknown York2	Vibration	Functional group	Frequency range given in literature (1)
GS1	VA10	VA11	VA12	PHS25	PHS26	PHS27	PHS55				
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1			cm-1
3276(s,b)	3333(s,b)	3333(s,b)	3339(s,b)	3297(s,b)	3282(s,b)	3291(s,b)	3319(s,b)	3308(m,b)	N-H stretch hydrogen bonded	peptide bond (trans-)	3320 - 3270(m)
3071(w)	nr 3070(s)	nr 3070(vw)		nr 3070(w)	nr 3070(w)	nr 3070(w)		nr 3080(sh)	amide II overtone	peptide bond (cis- and trans-)	3100 - 3070(w)
					2961(m)		2963(m)	2960(s)	C-H stretch	methyl group	2962 ± 10(s)
2942(w)	2938(w)	2940(w)	2944(w)	2926(m)	2927(m)	2922(m)		2929(s)	C-H stretch	methylene group	2926 ± 10(s)
				2855(w)		2854(w)	2878(w)	2870(s)	C-H stretch	methylene group	2853 ± 10(s)
									C-H stretch	methyl group	2872 ± 10(s)
	nr 2100(w,b)	2132(w,b)	2129(w,b)						unassigned		
1648(s)	1649(s)	1673(s)	1698(vs)	1659(s)	1652(s)	1658(s)	1661(s)	1662(s)	amide I C=O stretch	peptide bond	1680 - 1630(s)
								1606(s)	COO- vibration anti-symmetric	ionized carboxylic acid	near 1600(s)
1554(s)	nr 1550(w)	1541(s)	1573(s)	1548(s)	1545(s)	1548(s)	1536(s)	nr 1550(sh)	amide II-coupled N-H deformation and C-N stretch	peptide bond	1570 - 1515(s)
	1510(s)								unassigned		
1449(m)	1454(s)	1452(s)	1472(s)	1451(m)	1450(m)	1451(m)	1449(s)	1454(s)	C-H deformation	methylene group	1465 ± 20(m)
									C-H asym. deformation	methyl group	1450 ± 20(m)
								1422(s)	COO- vibration symmetric	ionized carboxylic acid	near 1400(s)
					1400(w)	1394(w)	1388(m)	1382(s)	C-H sym. deformation	methyl group	1380 - 1370(s)
1309(m)	1335(m)	1338(m)	1344(m)				1341(m)		unassigned		

TABLE 8.1 contd.

Frequency values and band assignments for proteinaceous materials

Albumen GS1 cm-1	Rabbit skin glue VA10 cm-1	Animal glue VA11 cm-1	Hide glue VA12 cm-1	Horn PHS25 cm-1	Horn PHS26 cm-1	Horn PHS27 cm-1	Tortoise-shell PHS55 cm-1	Unknown York2 cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
								1270(s)	amide III-coupled	peptide bond	1305 - 1200(m)
	1238(s)	1237(s,b)	1256(m) 1203(m)	1234(m)	1233(m)	1235(m)	1235(s)	1233(s)	N-H deformation and C-N stretch		
								1177(s)	unassigned		
	nr 1100(w)			nr 1100(sh)	nr 1100(sh)	1104(w)	1107(w)	1116(s)	unassigned		
		1084(s)	1089(m)						unassigned		
1049(m)	nr 1050(w)			nr 1050(sh)	nr 1050(sh)	1046(w)	1044(w)	1037(m)	unassigned		
nr 1000(sh)		nr 1000(w)						961(m)	unassigned		
nr 940(sh)		nr 930(vw)					921(w)	925(m)	unassigned		
								900(m)	unassigned		
	nr 875(w)							874(m)	unassigned		
		nr 850(vw)							unassigned		
	nr 810(w)						nr 800(sh)	820(s)	unassigned		
							nr 750(sh)	754(m)	unassigned		
								701(m)	unassigned		
								654(m)	unassigned		
								556(m)	unassigned		

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near